

COPPER CENTERS
IN
SEMICONDUCTORS
FOR
OPTOELECTRONICS

NILS
KULLENDORFF

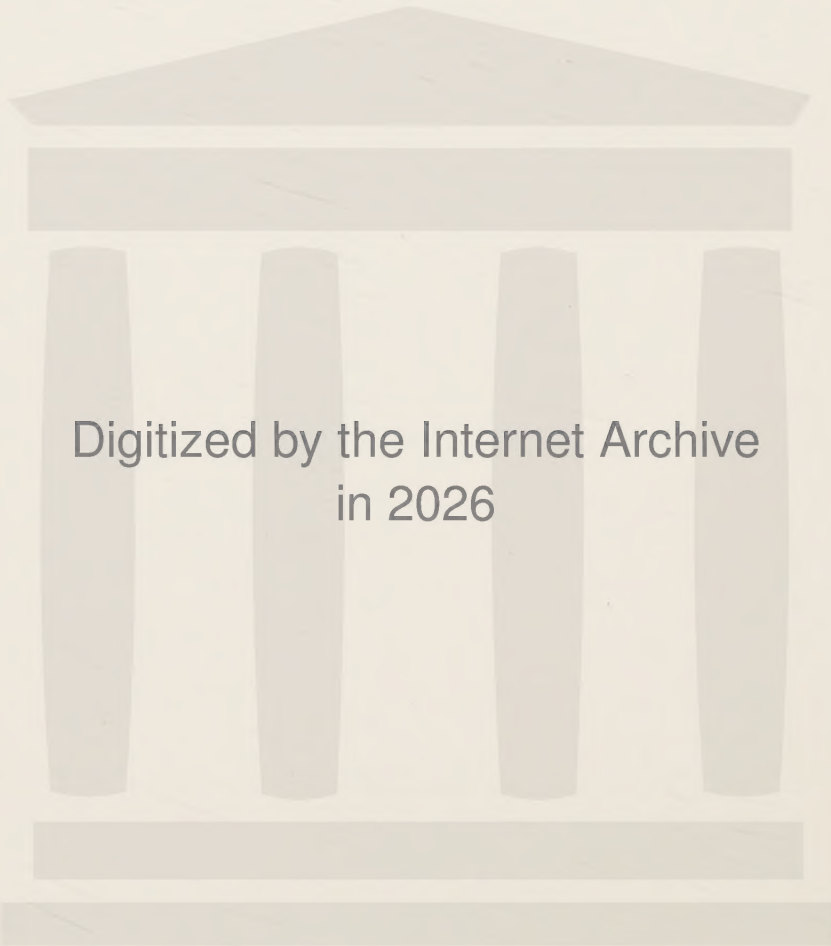


DEPARTMENT
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COPPER CENTERS IN SEMICONDUCTORS FOR OPTOELECTRONICS

by

Nils Kullendorff

Department of Solid State Physics, University of Lund, Box 725,
S-220 07 LUND, Sweden

This thesis is a study of copper related deep levels in some semiconductors used in optoelectronic applications. The work is presented in the following five papers:

- I Photocapacitance studies of CdS:Cu
 J. Appl. Phys. 52, 3405 (1981)
- II Electron capture cross-section in copper doped CdS
 Solid State Commun. 35, 727 (1980)
- III A steady-state constant capacitance method for the characterization
 of deep energy levels in semiconductors
 J. Appl. Phys. 51, 5852 (1980)
- IV Electrical and optical properties of copper doped zinc oxide
 Manuscript
- V Properties of copper related deep centers in III-V semiconductors
 Manuscript

Co-authors are H. G. Grimmeiss (I-III), R. Broser (I), E. Janzén
(II), R. Helbig (IV), L. Jansson (V), and L.-Å. Ledebø (V).

This summary of the thesis is divided into the following sections:

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Introduction

The understanding of impurity and defect centers in non-metallic solids is one of the oldest and most persistent problems in solid state physics, in spite of extensive efforts both on its experimental and theoretical aspects. The most important incentive for these efforts is the decisive role of point defects in semiconductors. By a controlled introduction of impurities in these materials the electrical conductivity can be chosen over the whole range from the isolating to the metallic extreme and the conduction can be chosen n- or p-type. These possibilities resulted in the invention of semiconductor devices such as the transistor which is the foundation of the electronic revolution. Impurity doping can also give rise to efficient luminescence, utilized in different types of display devices, and to enhanced recombination, utilized in fast switching devices.

Besides these highly desirable properties impurity and defect centers also are the origin of a number of unwanted processes in semiconductor devices. These include leakage currents in transistors and diodes, enhanced recombination reducing the output of solar cells as well as non-radi-

ative recombination lowering the efficiency of display devices and semiconductor lasers.

The impurities used to increase the conductivity of semiconductors generally give rise to shallow energy levels while other impurity-related processes in most cases are due to deep levels. Donor and acceptor levels close to the conduction respectively valence band of the host material are classified as shallow while the contrary holds for deep levels. In principle there is no well-defined distinction between these two categories, but in practice almost all impurity or defect levels can be classified according to these two groups in a straight-forward manner. As a rule of thumb the energy 0.1 eV can be used as a dividing line.

Shallow donors in group IV semiconductors, such as silicon, are created by impurities from group V of the periodic table while shallow acceptors are obtained from group III elements. In both cases it is assumed that the impurity atom takes an isolated substitutional site, which is normally found for these impurities. In compound semiconductors the two possible types of substitutional sites must be taken into account. In GaAs for example group II elements on Ga-site give rise to shallow donors while group IV elements give rise to shallow acceptors. On As-site group IV elements create shallow acceptors on the other hand while group VI elements create shallow donors.

An atom of an element from the same column of the periodic table as the one it replaces has the same number of valence electrons as the latter and gives rise to an isoelectronic center. A complex center which has the same total number of valence electrons as the atoms it replaces also is classified as isoelectronic. Isoelectronic centers can introduce donor or acceptor levels or no levels at all in the band gap of the host material. In the last case they still can be important in applications since efficient electron-hole pair recombination sometimes takes place at such centers.

Elements from other columns of the periodic table either give rise to deep levels or no levels at all in the gap. Atoms of these elements can take both substitutional or interstitial sites or associate with other impurities or native defects to form complex centers. Elements expected to give rise to shallow levels can also create deep levels by such defect reactions.

For a recent review of the electronic structure of impurities and other point defects in semiconductors see ref. 1.

Among the impurities giving rise to deep levels copper is one of the most common. Copper is a rapid interstitial diffuser in most semiconductors already at comparatively low temperatures² and since it is often present in the starting material, the dopants and the processing environment it is often found as a contaminant in these materials. This fact is one of the most important motives for this thesis.

Since copper mainly creates acceptor levels it tends to compensate n-type material. This property and the fact that copper gives rise to efficient luminescence in some materials are the main reasons for deliberate copper doping. Even though these effects are known the underlying mechanisms are often insufficiently understood which is another important motive for the thesis.

According to the discussion above copper is expected to give rise to shallow acceptors when occupying group II sites in II-VI compounds. Contrary to this expectation these acceptors are deep and thus constitute one of the few exceptions from these statements. The reasons for this anomaly are discussed in the next section.

Copper centers in II-VI compounds

II-VI compounds have, as a group considered, larger band gaps and are more ionic than III-V and group IV semiconductors. Efficient luminescence is often observed in these materials and utilized in commercial phosphors based on ZnS. Such phosphors are used in cathodoluminescence applications, electroluminescent display devices and phosphorescent paint. The efficient luminescence and the fact that some of the emissions cover the blue region of the visible spectrum, which cannot be reached using materials with smaller band gaps, have incited extensive efforts to develop light-emitting diodes (LEDs) based on wide-gap II-VIs. The efforts have been eluded however, by the fact that low-resistive bipolar conductivity has not been achieved in these materials.

Among other applications of II-VI compounds photoconductors and solar cells should also be mentioned. The high sensitivity of CdS-based photoconductors and the possibility to match their spectral response to daylight by appropriate processing have made them frequently used for light detection and measurement.

CdS also is used in $\text{Cu}_2\text{S}/\text{CdS}$ heterojunction solar cells which reach an efficiency of more than 8 % and can be fabricated at comparatively low costs³. These cells have been found to degrade however, primarily because of diffusion of copper from the Cu_2S layer into the CdS. Photoelectrochemical solar cells (PECs) can be based on several II-VI compounds and reach fairly high efficiencies but are often subject to degradation³.

As mentioned above Cu is a common impurity in many semiconductors and this is especially true for II-VIs. Specific purification procedures have been developed to reduce the Cu content^{4,5}. When introduced in the material Cu gives rise to a number of different centers. In EPR studies of ZnS nine different Cu-related centers were observed⁶ and in luminescence of ZnS

three dominant Cu centers are seen⁷. Studies of optically detected magnetic resonance (ODMR) in ZnSe also indicate several Cu-related centers⁸.

Since isolated Cu on cation site seems to be the dominant electrically active Cu-related center in many II-VIs and since this center is mainly discussed in the papers of this thesis the following discussion is restricted to this case. In a recent paper by Robbins the Cu_{Zn} acceptor in the Zn-VI compounds is systematically reviewed⁹. Fig. 1 is taken from this paper though some alterations are made here.

In materials with a low valence band, with ZnO as the extreme, the Cu d-levels fall in the band gap. This situation can alternatively be described as a transfer of the tenth d-electron to the second 4s bonding orbital of Cu caused by the large electronegativity of the anions. In the free Cu atom the transition $3d^{10}4s \rightarrow 3d^9 4s^2$ requires only 1.4 eV and thus can be energetically favourable in a crystal environment if the sp^3 bonds are completed.

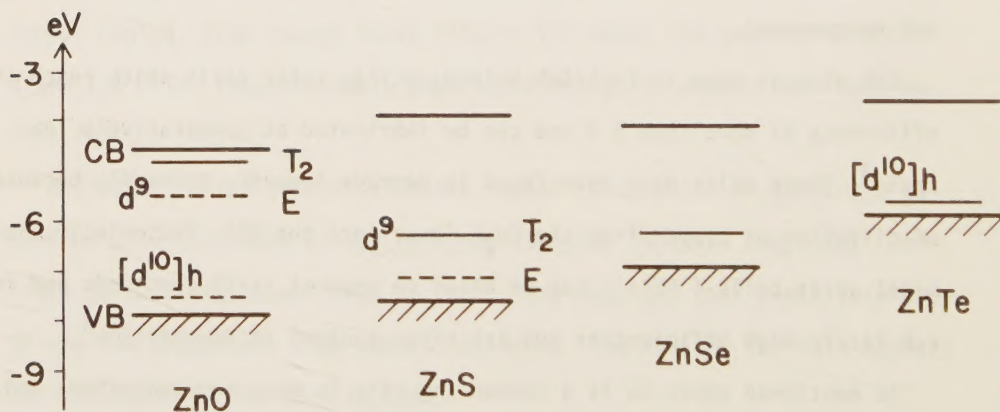


Fig. 1 Energy levels of Cu_{Zn} in the Zn-VI compounds (from ref. 9).

In materials with a high valence band, such as ZnTe, the Cu d-levels fall below the band edge and Cu_{Zn} becomes a simple acceptor with a $3d^{10}4s$ configuration. Some d character is mixed into the ground state wave function however and makes the acceptor deeper, $E_A=149$ meV, than other shallow acceptors in ZnTe, $E_A=50-70$ meV¹⁰. ZnS and ZnSe are intermediate cases between the extremes as can be seen in Fig. 1.

The transition from deep d-hole acceptor to comparatively shallow acceptor is a consequence of the specific electronic properties of Cu and the host materials and has no direct analogue, with the possible exception of Ag and Au in II-VIs. However, the $4d^{10}5s \rightarrow 4d^95s^2$ transition in the free Ag atom requires 3.7 eV and in the case of Au the ionic radius might be too large to favour a substitutional site.

The different types of excited states are also dependent on the position of the Cu d-levels relative to the valence band of the host⁹. In tetrahedral (T_d) symmetry a d-hole orbital is split into a t_2 orbital (ground state) and an e orbital (excited state). The splitting (Δ) is about 0.8 eV in all the II-VIs in which it can be measured. In ZnO these levels are high above the valence band and additional excited hole states close to the valence band are observed. These states corresponds to a $3d^{10}4s$ configuration with some d-character mixed into it and seem to be analogous to the ground state of $\text{ZnTe:Cu}_{\text{Zn}}$. In the nomenclature of Robbins they are denoted charge transfer (CT) states. In ZnS no CT states are seen, but in this case the e-level has approximately the same distance to the valence band as is expected for CT states. It thus seems plausible that the e-states have some admixed character of CT states. It should be noted that the infrared absorption corresponding to a $t_2 \rightarrow e$ transition has a different appearance in ZnO and ZnS^{11,12} and that the reverse transition is non-radiative in ZnO but radiative in ZnS¹³.

In ZnSe the e-level falls just below the valence band edge if the same value of Δ is assumed as observed in the other II-VIs. The photoionization cross section of holes for ZnSe:Cu indeed reveals a broad but pronounced peak at an energy close to the band edge, indicating a resonant level at this energy¹⁴. Strong interaction with valence band states is expected for such a resonance and no structured absorption or emission of intra d-shell character has, to the knowledge of the author, been reported for this center.

Finally the controversies pertaining to the identification of copper centers in CdS should be mentioned. The "sensitizing" centers in CdS photoconductors induce quenching spectra similar to the photoionization cross section of holes for the dominant copper center¹⁵. However, measurements of electron capture clearly demonstrate that these centers are not identical^{16,17}. At present it is not clear whether the similarity is just a coincidence or if it has a deeper physical explanation. The infrared emission of CdS:Cu has been attributed to both Cu_{Cd} ¹² and native defects or associates involving Cu and native defects¹⁸. The emission is very similar to the corresponding emission in ZnS which has been shown to be due to Cu_{Zn} by Zeeman analysis¹⁹⁻²¹. The situation is further complicated by the fact that Cu is a common residual impurity in II-VIs as mentioned above and that it plays an important role in the general defect chemistry in these materials.

The suggestion of a Cu_{Cd} center in Sec. V of paper I is to a large extent based on the close correspondance between the spectra reported in this paper and the optical absorption spectra obtained in ZnS doped with Cu using neutron transmutation, i.e. the reaction $\text{Zn}^{64} + n \rightarrow \text{Zn}^{65} \rightarrow \text{Cu}^{65}$ is utilized²². In this context it is interesting to note that Bube, who has discussed the role of copper and sensitizing centers, recently published a paper in which photocapacitance spectra obtained in $\text{Cu}_2\text{S}/\text{CdS}$ solar cells and very similar to ours are ascribed to Cu_{Cd} ²³.

Copper centers in III-V compounds

The possibility of low-ohmic bipolar conduction in III-V compounds makes them more flexible for applications than the II-VIs. A variety of devices can be based on III-Vs: optoelectronic devices such as LEDs, semiconductor lasers and photodiodes, microwave devices such as Gunn oscillators and high-frequency field-effect transistors (FETs), high-performance solar cells and high-speed logic circuits to name the most important categories. The high electron drift velocity of GaAs is utilized in microwave FETs and high-speed logic while the special band structure of GaAs and InP is utilized in Gunn devices.

With the exception of some excitons Cu in III-V compounds gives rise to either non-radiative recombination or broad featureless infrared emissions why it has been less extensively studied than in the II-VIs. The technological interest of Cu in III-Vs is primarily of negative nature, i.e. the problem is how to avoid reduced device performance due to copper related centers.

To the knowledge of the author no unified description of Cu-related deep levels in III-V semiconductors has been presented in the literature and therefore an attempt to demonstrate some general trends is presented in paper V of this thesis. Since Sec. IV of this paper includes a general discussion of the subject the discussion is not repeated here. The data presented in paper V and references therein show that the two dominant Cu-related deep levels, denoted Cu_A and Cu_B , in InP, GaP, GaAs, AlAs and some alloys of these have approximately the same positions relative to the vacuum level in all the materials. A level scheme taken from this paper is presented in Fig. 2. This observation and some further similarities observed lead to the proposal that the two centers retain their respective structure when passing from one material to another, i.e. each

center is of a common nature in the different III-V materials. No unambiguous identification of the centers is possible at present but the importance of anion vacancies is shown in the literature²⁴⁻³⁰ and the symmetries C_{3v} and C_{2v} respectively are deduced from exciton luminescence³¹.

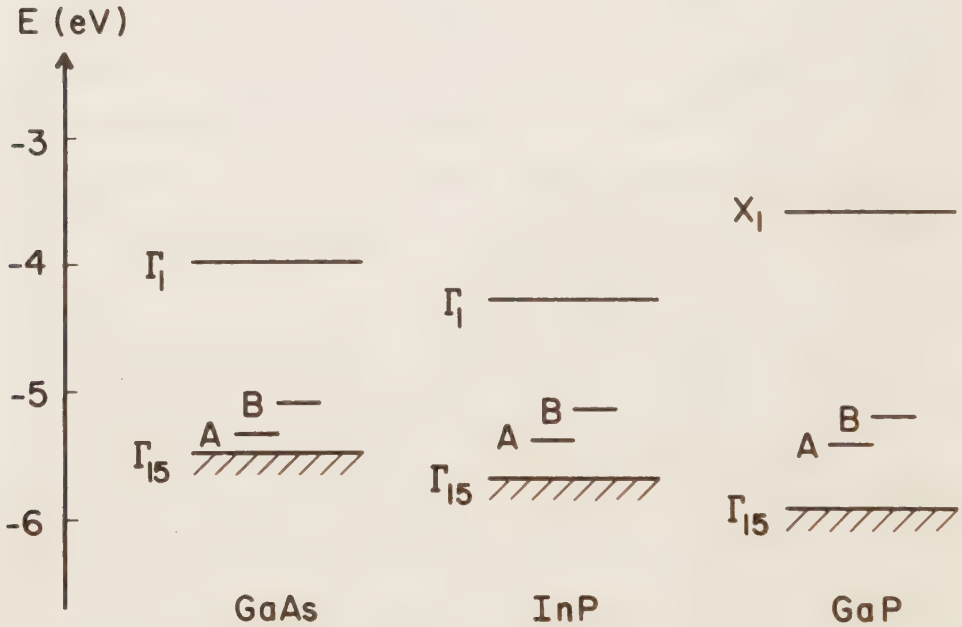


Fig. 2 Energy levels of Cu in some III-V compounds (from paper V of this thesis).

Experimental techniques

The results presented in this thesis are mainly obtained using junction space charge spectroscopy. In ref 32 and 33 these and related techniques are reviewed. The possibility to study a specific impurity-related excitation or deexcitation process separately, unaffected by other electronic transitions or material parameters is a very important advantage of junction methods compared to measurements in bulk material. This possibi-

lity makes the evaluation of experimental data straightforward and absolute values of deep level parameters easy to obtain.

A particularly convenient space charge technique for measuring thermal excitation and, in some cases, free carrier capture, is deep level transient spectroscopy (DLTS), originally suggested by Lang³⁴. This technique has become a wide-spread method both for routine characterization of semiconductors and for scientific defect studies. An elegant review of DLTS is given in ref. 35.

A drawback of optical space charge spectroscopy, i.e. photocapacitance measurements, is the time-consuming measurement and evaluation procedures. The work presented in paper I also resulted in the idea of the faster method presented in paper III. A modified version of this method was employed for a high-resolution measurement presented in paper V.

For photoionization measurements at photon energies smaller than 0.3 eV conventional light sources become inefficient. In this spectral range Fourier transform spectroscopy³⁶ is an attractive alternative, which can be chosen both for optical absorption and photoconductivity studies³⁷. This approach was employed for some measurements on ZnO:Cu presented in paper IV. Fourier transform spectroscopy is reviewed in ref. 36.

Levels close to a band edge can also be troublesome to study using a standard DLTS set-up since the thermal excitation become too fast. In this case admittance spectroscopy, first suggested by Losee³⁸, is an alternative. A drawback of the method is the smaller sensitivity compared to DLTS. Admittance spectroscopy was employed to measure thermal hole emission from the GaAs:Cu_A level, presented in paper V.

Luminescence measurements are not reported in the papers of this thesis but since they are frequently quoted they are briefly discussed here. A variety of impurity-related phenomena can be studied by luminescence, such as

bound excitons, donor-acceptor pair emission, free-to-bound emission and internal d- and f-shell transitions in transition metal respectively rare earth impurities.

Not only recombination but also excitation can be studied if photoluminescence excitation (PLE) spectroscopy is employed³⁹. In PLE measurements narrow band excitation light is swept over the spectral region of interest while the intensity of the emitted light is monitored. By this technique e.g. photoionization cross sections of deep levels can be obtained. Photoluminescence quenching (PLQ) spectroscopy³⁹ is another technique to obtain photoionization cross sections, in general the cross section which corresponds to the non-radiative recombination step.

If narrow zero-phonon lines are observed the Zeeman effect can be employed to explore the local symmetry of a defect which is of decisive importance for identification. If no sharp lines are available the symmetry can often be obtained by the ODMR technique. ODMR=optically detected magnetic resonance is reviewed in ref. 40. When using this method an electron paramagnetic resonance is monitored via the induced intensity or polarization variations of the recombination emission of the resonant center. An important feature of ODMR is the direct link between the resonance and the optical emission which simplifies the defect identification.

A similar link between a paramagnetic resonance and a capture or excitation process is very desirable for non-radiative centers. A combination of EPR and the electrical methods mentioned above is possible in principle but the technical problems are probably severe.

Theory

The theory of electronic impurity and defect states in semiconductors is still at an early stage of development in spite of decades of hard work on the problem. The extremes of very delocalized and very localized states, i.e. shallow donors or acceptors and internal d- or f-shell transitions in transition metal or rare earth impurities respectively were early found to be manageable. The shallow states were given a crude description by a simple hydrogenic model, scaled by the dielectric constant and the effective mass of the corresponding charge carrier. The theory was accordingly called the effective-mass theory (EMT) or the Kohn-Luttinger effective-mass theory after its main inventors^{41,42}. Refinements of the theory have been made to take into account the effects of crystal anisotropy⁴³, multi-valley splitting in materials with indirect band gap⁴³ and the complications due to the p-like valence band top in cubic materials⁴⁴⁻⁴⁶. The EMT can now be considered to give a satisfactory description of shallow donors and acceptors (and the excited states of some deep centers⁴⁷).

In the EMT the impurity potential is treated as a perturbation of the electron states of the host material. In the opposite case of internal d- or f-shell transitions the host material is considered to act as a perturbation on the atomic-like states of the impurity ion core. In the simplest approach, the crystal field theory^{48,49}, the host material is represented by the nearest neighbours of the impurity ion. These neighbours are approximated with point charges and the resulting electrostatic potential acts as a perturbation splitting the free ion levels. Using group theory qualitative level schemes and symmetry properties of the corresponding wave functions are easily derived.

While f electrons of rare earth impurities are well shielded from the crystal surroundings the shielding of d electrons of transition metal im-

purities is less complete. In the next order of approximation, the ligand field theory^{48,49}, hybridization between the d orbitals and the s and p orbitals of the neighbours therefore is taken into account. Symmetry arguments are used to construct the appropriate combinations of orbitals and the theory can be described as a qualitative molecular-orbit theory of the impurity ion and its neighbours.

The crystal and ligand field theories are essentially qualitative and absolute level splittings are usually derived from experiments. They give little or no information on the energy position of the impurity levels relative to the energy bands of the host which often is of great importance in applications. To obtain this position qualitative cluster calculations are required. In the case of Cu in II-VIs such calculations have been performed by Müller and Scherz and give results consistent with the discussion on p. 6-8 above⁵⁰.

It is obvious that a general theory of impurity and defect centers in semiconductors should treat neither the defect potential nor the host material as a perturbation but treat them on an equal footing. Several attempts to develop such a theory have been presented. To the opinion of the author the most promising approach is the Green's function scattering theoretic method⁵¹⁻⁵⁴. This method not only gives the energy levels in the band gap but also the local density of states within the bands. Using this information e.g. photoionization cross sections can be calculated or the local charge distribution which in turn can be used to obtain vibrational properties. The theory is still in its infancy but has recently been extended to describe transition metal d orbitals⁵⁵.

Drawbacks of the Green's function methods are the extensive computations required and the difficulty to get simple semiquantitative results. If less detailed information is needed the $X\alpha$ -scattered-wave method can be an economic approach, at least for strongly localized electron states¹. This met-

hod has been used to calculate the energy levels of several transition metal impurities in III-V compounds⁵⁶ and in silicon⁵⁷.

The majority of calculations on impurity and defect states reported in the literature deals with systems of simple geometrical structure such as isolated substitutional impurities, isolated interstitials or isolated vacancies. It is known from experiments that a large number of impurity and defect centers, among them many technologically important systems, have a more complicated microscopic structure. Association between two or several impurity atoms or between impurity atoms and native defects often occur. Structures such as split-interstitials and bond-interstitials⁵⁸ can be more stable than substitutionals or interstitials. In addition to simple vacancies divacancies and multivacancies occur. Strong lattice relaxation is expected in most of these cases and can reduce the symmetry of the systems. A successful theory of impurity and defect centers accordingly must be applicable to such complicated and distorted centers as well as the simpler centers mentioned above. though the difficulties are considerable they are, to the opinion of the author, probably less severe than the difficulties encountered in a general experimental exploration of the microscopic structure and electronic properties of these centers.

Summary of the papers

I Photocapacitance studies of CdS:Cu

In this paper photocapacitance measurements on the dominant deep center in Cu diffused CdS are reported. The results are interpreted in terms of a deep acceptor with an excited hole state. Optical emission of both holes and electrons as well as internal transitions followed by thermal hole emission have been studied. The kinetics of the electron traffic of the center is

thoroughly analyzed and studied experimentally. Absolute values of photoionization cross sections have been obtained for both holes and electrons. The thermal activation energy for the photothermal hole emission via the excited hole state into the valence band has been determined. An interesting temperature dependence of the magnitude of the photoionization cross section of holes and an interesting thermal broadening of the photoionization cross section of electrons are reported. The results are related to previous investigations of optical absorption, luminescence, photoconductivity and photo-Hall effect.

Since ambiguous band models of Cu in II-VIs are found in the literature the relation between the ionization energies, the energy levels of the total ion core and the "effective" one-particle levels which have to be used in a band model is clarified in the discussion part of the paper.

II Electron capture cross section in copper doped CdS

This study is an extension of the work reported in paper I. An improved contacting technique resulted in diodes with negligible series resistance suitable for capture measurements using a high-frequency capacitance bridge with bias-pulse facilities. The electron capture cross section of the dominant center was measured in the interval 150-270 K using the pulse-train technique. It was found to be temperature independent and to have the value $1.2 \cdot 10^{-20} \text{ cm}^2$. The magnitude and temperature independence are consistent with radiative capture by a neutral center and thus with the model in paper I.

III A steady-state constant capacitance method for the characterization of deep energy levels in semiconductors

The work presented in paper I also resulted in the idea of the steady-state constant capacitance (SSCC) method presented in this paper. The method is

suitable for samples with a high deep level concentration and makes both measurement and evaluation procedures considerably less time-consuming and more straightforward than in the case of conventional photocapacitance transient spectroscopy. A further advantage is the possibility of photoionization cross section measurements even in the presence of moderate thermal excitation processes which can be troublesome using capacitance transients.

The feasibility of the method is exhibited by presenting data on the dominant centers in copper doped CdS and ZnSe.

IV Electrical and optical properties of copper doped zinc oxide

In this paper results on Cu doped ZnO obtained by junction space charge and Fourier transform spectroscopy are reported. The dominant Cu_{Zn} acceptor, close to the conduction band edge, has been investigated concerning thermal electron emission, electron capture, optical absorption and photoconductivity. The absorption spectra exhibit pronounced structure which is interpreted in terms of resonances in the conduction band due to final-state interaction between the excited electron and the remaining hole in the Cu d-shell. A small transition probability to undistorted s-like band states is assumed to make these resonances dominant. The photoconductivity spectrum is supposed to be modified by surface effects since the current is believed to flow within an accumulation layer close to the surface. Previous photoconductivity measurements are discussed in this context.

For a deep unidentified donor optical and thermal electron emission have been measured using capacitance spectroscopy. The concentration of the donor is found to rise dramatically close to the surface which might indicate a relation to excess zinc. The photoionization cross section has a pronounced structure also in this case, indicating the existence of both discrete excited states and resonances near the band edge. The nature of these is

more uncertain since the center is not identified. A model of a $\text{Cu}_{\text{Zn}}\text{Zn}_i$ complex with hybridized d and donor orbitals is suggested.

At low temperatures a third level, possibly due to the 0.16 eV native donor or the second donor state of Zn_i , is observed in photoconductivity. The spectrum is very irregular which is interpreted as the combined action of excited states and surface effects.

V Properties of copper related deep centers in III-V semiconductors

The work presented in this paper started as an investigation of deep Cu related levels in InP using junction space charge spectroscopy. Photoionization cross sections of holes and electrons, thermal hole emission rates and capture cross sections were obtained for the dominant centers. To the knowledge of the author no results on Cu centers in InP have been reported in the literature and our data thus are of a considerable novelty value. One of the ionization spectra also exhibits an interesting structure which is discussed in the paper. A possible explanation is Fano resonances due to LO phonon replica of discrete electronic transitions and the onset of transitions to the split-off band.

During the work it became obvious that close similarities exist between Cu centers in different III-V materials. Results on Cu diffused GaAs were therefore incorporated in the paper and previous work on other III-V systems cited to obtain data for a unified description of deep Cu levels in III-Vs. The main conclusion is that two dominant Cu-related deep levels, denoted Cu_A and Cu_B , are found in all III-Vs investigated and that these levels have approximately the same absolute energies, i.e. the same positions relative to the vacuum level in all the materials. A close similarity is therefore suggested between the Cu_A centers in the different materials and analogously for Cu_B . In other words: both centers are assumed to retain their respective structure

when passing from one material to another. This proposal is further supported by some additional similarities observed, namely phonon related structure in the photoionization cross sections of holes for Cu_A in InP and GaAs.

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ELECTRICAL AND OPTICAL PROPERTIES OF COPPER DOPED ZINC OXIDE

N. Kullendorff

Department of Solid State Physics, University of Lund, Box 725,
S-220 07 LUND, Sweden

R. Helbig

Institut für Angewandte Physik, Universität Erlangen-Nürnberg,
D-8520 ERLANGEN, FRG

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Abstract

Copper doped zinc oxide has been studied using junction space charge and Fourier transform spectroscopy. The dominant Cu_{Zn} acceptor, close to the conduction band, has been investigated concerning thermal electron emission, electron capture, optical absorption, photoconductivity and photo-capacitance. The absorption spectrum exhibits pronounced structure indicating the existence of resonances in the conduction band.

For a deep unidentified donor optical and thermal electron emission have been measured. The ionization spectrum exhibits pronounced structure also in this case, indicating the existence of both discrete excited states and resonances near the conduction band edge. The results on Cu_{Zn} and the deep donor are compared to earlier photoconductivity data and the role of surface effects is discussed.

At low temperatures a third center, probably the 0.16 eV native donor, is observed in photoconductivity.

I. Introduction

Copper doped zinc oxide has recently been subject to both experimental and theoretical work owing to its interesting optical and electronical properties¹⁻³. The dominant copper-related center, generally accepted to be a substitutional Cu_{Zn} acceptor, gives rise to both green luminescence (hole transition $\text{CT} \rightarrow t_2$ in Fig. 10) and corresponding optical absorption as well as infrared absorption (hole transition $t_2 \rightarrow e$ in Fig. 10). In all cases narrow zero-phonon lines have permitted Zeeman experiments giving detailed information on symmetry properties and g-tensors¹⁻⁶. Infrared absorption as a function of varying Fermi level has been studied to establish the position of the acceptor ground state relative to the energy bands of the host material⁷. From these studies the level was found to be located about 0.19 eV below the conduction band edge, which can be compared to the band gap of ZnO which is 3.4 eV at low temperature.

Recently infrared luminescence has been reported and is found to originate from another, probably more complex copper-related center¹. This discovery might be significant for other II-VI compounds as well, as discussed in ref. 1.

Electron paramagnetic resonance has also been studied both for Cu_{Zn} ⁴ and for other copper-related centers^{8,9}. For the former the results are fully consistent with Zeeman data² and make, together with these, an unambiguous identification possible.

Electrical conductivity and Hall effect measurements have also been performed to locate the energy levels of Cu_{Zn} and give results consistent with those mentioned above^{7,10}. Other copper-related centers have been discussed in this context¹¹.

In spite of all experimental data important information, difficult to obtain with the techniques mentioned, still has been lacking. The recent extension of junction space charge spectroscopy to II-VI compounds¹²⁻¹⁵

and the use of Fourier transform spectroscopy have made possible further investigations presented here. These include for Cu_{Zn} thermal electron emission (electron transition $t_2 \rightarrow \text{CB}$ in Fig. 10), electron capture (reverse transition), optical absorption, photoconductivity (PC) and photocapacitance corresponding to optical electron emission (electron transition $t_2 \rightarrow \text{CB}$), and for a deep unidentified donor thermal and optical electron emission (electron transition $\text{DD} \rightarrow \text{CB}$) and concentration profile.

The optical spectra exhibit pronounced structure for both Cu_{Zn} and the deep donor, indicating the existence of resonances, and for the donor also discrete excited states, near the conduction band edge.

At low temperatures a third level, closer to the conduction band, is observed in PC (electron transition $\text{ND} \rightarrow \text{CB}$).

Finally we want to mention some applications of copper doped (or copper contaminated) zinc oxide. Since the "Cu-green" emission in ZnO is due to bound-to-bound transitions the decay time is short, $< 1 \mu\text{s}$ ¹⁶, in contrast to the case of "Cu-green" emission in ZnS which is due to donor-acceptor pair recombination and therefore has a slower decay^{17,18}. In fast cathodoluminescence applications $\text{ZnO}:\text{Cu}$ thus has an obvious advantage.

Light-emitting diodes and AC electroluminescent devices utilizing the green emission have also been reported^{19,20}. In these references this band is not explicitly attributed to copper although it is now generally accepted to be caused by Cu_{Zn} ²¹.

Since copper gives rise to deep acceptors it compensates low-ohmic ZnO and makes the material high-resistive. To obtain very high-ohmic material however, the Cu_{Zn} acceptor is too close to the conduction band and other acceptors, Cu-related or of different origin, are required¹¹.

II. Sample preparation

The investigated crystals were grown by a vapour phase reaction method²² with Cu-doped polycrystalline ZnO as starting material. Most of the crystals were hexagonal needles with well shaped prism faces (parallel to the crystal c-axis). In some cases (see below) crystals of pyramidal form with well developed (0001) faces (oxygen faces) were used. The cited impurity concentrations (Cu, Al) were determined using atomic absorption spectroscopy.

Schottky diodes of good quality were fabricated on crystals with a free electron concentration of $8 \cdot 10^{15} \text{ cm}^{-3}$. Gold was vacuum evaporated onto prism faces without surface pretreatment. Ohmic contacts were made of liquid GaAl covered with colloidal silver. Electrical contact with the gold layer was established with a thin gold or platinum wire.

The crystals had previously been exposed to air at room temperature for a long time and are therefore assumed to have been covered by physisorbed and chemisorbed oxygen²¹. The existence of surface states on the crystals, probably due to adsorbed oxygen, which become interface states in the Schottky diodes was found to be essential for the diode quality. Any chemical or mechanical treatment of the surface before gold evaporation resulted in poor diode characteristics.

These states also had a decisive influence on the photoelectronic properties of the diodes. Any process creating free holes within the depletion region such as excitation over the band gap, excitonic absorption or two-step impurity excitation resulted in a dramatically increased capacitance. We interpret this process as hole capture by interface states resulting in photochemical surface reactions lowering the barrier height. Possible reactions are photodesorption of oxygen and photolysis, eventually followed by diffusion processes²¹. As a consequence no hole emission from deep levels could be studied.

Illumination with band gap light in vacuum resulted in severe degradation of the diodes. The recovery was slow and required the presence of oxygen. This is consistent with the assumption of interface states related to oxygen which might be released after hole capture and might diffuse through the gold layer. This assumption is also supported by the fact that vacuum storage in darkness also degraded the diodes but to a lesser extent than under illumination. A similar behaviour is reported in ref. 22.

Since the crystals had been exposed to daylight during long periods before the gold evaporation photodesorption of oxygen is expected to have occurred. Excess zinc at the surface is therefore expected to have diffused into the bulk. Such a diffusion might be the origin of the unusual distribution of the deep donor in Sec. III B.

Photoconductors were made of the same material as the Schottky diodes and ohmic contacts made in the same manner as for those. The prism faces were exposed to the incident light. The photoconductors exhibited a high sensitivity for band gap light both at 80 and 300 K²¹.

Optical absorption measurements were performed on high-resistive crystals with a copper concentration larger than 10^{18} cm^{-3} . In this case the polar faces were exposed to the light.

III. Experimental results

A/ The dominant Cu_{Zn} acceptor

The thermal emission rate of electrons e_n^t was measured using capacitance transient techniques^{23,24}. Since the concentration of this level was about $5 \cdot 10^{15} \text{ cm}^{-3}$, i.e. not small compared with the shallow donor concentration, the constant capacitance method was used in an attempt to get an exponential time dependence of the transients^{25,26}. At higher temperatu-

res however, deviations from exponentiality was found even with this technique. We therefore used straightforward capacitance transients and defined the time constant τ by eq.

$$\Delta C(\tau) = \Delta C(t=0)/e, \Delta C(t) = C(t)-C(t=0) \quad (1)$$

with a small correction for the large deep level concentration.

The measurements were performed using a Leybold-Heraeus gas flow cryostat, a Boonton 72 BD capacitance meter and a Nicolet Explorer III digital oscilloscope. The feed-back system for keeping the capacitance constant was constructed by one of us (NK).

An Arrhenius plot of e_n^t divided by the squared temperature T^2 is shown in Fig. 1. The slope corresponds to an energy of 0.193 eV.

The electron capture cross section σ_n was obtained using a single-shot version of the standard DLTS capture cross section measurement²⁷. The magnitude of the electron emission transient was monitored after a fast train of short filling pulses. When the number N of pulses in the train is changed this magnitude $\Delta C(N)$ varies according to eq.

$$\Delta C(N) = \Delta C(N \rightarrow \infty)(1-\exp(-c_n n N t_p)), \quad (2)$$

where t_p is the pulse width, $c_n = v_t \sigma_n$, $v_t = \sqrt{(3kT/m_n^*)}$ is the thermal velocity of the electrons and n is the free electron concentration which was obtained from C-V curves. To obtain fast pulses it was necessary to disconnect the capacitance meter during the pulse train which was made by fast switching relays.

Also in this case deviations from exponentiality was observed. The large deep level concentration causes deviations not only by non-linear capacitance response (see above) but also because the free electron concen-

tration changes during the filling sequence as a considerable amount of the electrons get trapped. A further reason is the tail of free electrons at the edge of the depletion layer²⁸. The influence of this tail was reduced however by reverse bias and by evaluating the capture for $N t_p < c_n n$. Instead of correcting for all the deviations the capture time constant $\tau_c = c_n n$ was defined analogously to the emission time constant, i.e. by eq.

$$\Delta C(N t_p = \tau_c) = \Delta C(N \rightarrow \infty)/e \quad (3)$$

An Arrhenius plot of σ_n is presented in Fig. 2. The slope corresponds to an energy of 0.028 eV.

The photoionization cross section of electrons σ_n^0 was found difficult to measure using conventional photocapacitance techniques since the level is situated less than 0.2 eV below the conduction band and no efficient broadband light source is available for these photon energies. Therefore we employed Fourier transform spectroscopy to measure the corresponding PC spectrum. A Nicolet 7002 FTIR spectrometer and a Keithley 427 current amplifier was used for this measurement. The spectrum of the globar was measured with a TGS- and a MCT-detector.

In Fig. 3 this PC spectrum is shown in a linear scale and in Fig. 4 the same data are shown in a semilogarithmic scale to more clearly visualize the ionization threshold at approximately 0.17 eV. Some structure in the spectrum can be seen and is further discussed in Sec. IV. The PC spectrum is similar to one reported in ref. 29-31 where it is assigned to surface states. As discussed in Sec. IV this assignment is questionable, though the surface probably has an important influence on the spectrum. The rise at higher energies (above 0.45 eV) is probably due to the deep donor which is assumed to contribute to the PC.

Using samples with a much higher copper concentration, 10^{18} - 10^{19} cm^{-3} , electron emission could also be observed as optical absorption. At such a high concentration the Fermi level is pinned to the Cu_{Zn} acceptor level and some of these centers are still available in the negative charge state making these absorption measurements possible. The FTIR spectrometer was used also in this case. In Fig. 5 the absorption spectrum at 8 and 78 K is presented. The absorption coefficient α is evaluated under the assumption of negligible reflexions at the surfaces. The Cu-related absorption could not be measured below 0.16 eV due to intrinsic two-phonon absorption ($2\hbar\omega_{\text{LO}}=0.144$ eV).

The ionization threshold at approximately 0.17 eV is clearly seen in Fig. 5. Pronounced structure appears above the threshold and indicates the existence of resonances in the conduction band. Since these peaks, except for the one at 0.27 eV, are not seen in the PC spectrum we conclude that transitions from these states back to the ground state are much more probable than release to the conduction band. Phonon replica of the peaks might give additional structure far above the ionization threshold. Further reasons for the differences between the absorption and PC spectra are the role of surface effects in the latter which is discussed in Sec. IV and is believed to be important in the 0.3-0.4 eV range, and different selection rules since they are obtained with light incident parallelly ($\vec{E} \perp \vec{c}$) respectively perpendicularly ($\vec{E} // \vec{c}$ and $\vec{E} \perp \vec{c}$) to the crystal c-axis. The deep donor is also assumed to contribute to the PC at higher energies as mentioned.

Even though photocapacitance could not be used to measure the spectrum of σ_n^0 it was employed to estimate the absolute value of σ_n^0 in the 0.3-0.4 eV range which was found to be of the order of 10^{-20} cm^2 , i.e. extremely small.

As mentioned above the concentration of Cu_{Zn} was approximately $5 \cdot 10^{15}$ cm^{-3} in the crystals used for the electrical measurements. The total Cu

concentration in these crystals, as determined by atomic absorption spectroscopy, was approximately $1 \cdot 10^{16} \text{ cm}^{-3}$.

B/ The deep donor

A second deep level, located a bit further down from the conduction band, could also be detected in the Schottky diodes. The concentration of this level was small in the interior of the crystals but rised dramatically towards the surface where it was comparable to the shallow donor concentration. After electron emission these centers gave an increase of the positive space charge close to the surface and are therefore concluded to be donors. Capacitance-voltage characteristics of a diode with these levels filled with electrons by forward bias pulses (a) and empty (b) are shown in Fig. 6 and clearly show this charge distribution. Thermal emission was utilized to empty the levels and therefore curve b is measured at somewhat higher temperature, 145 K, than curve a which is measured at 129 K. Since the barrier height of the diode was slightly decreasing with increasing temperature a small parallell displacement of the curve is superposed on the change due to the deep donor.

As discussed in Sec. II zinc is expected to have diffused into the crystal from the surface. The concentration profile of the deep donor thus suggests a relation to excess zinc. Isolated interstitial zinc is a shallow donor³⁶⁻³⁸ and a more complex center is therefore required. This might be a complex involving zinc and another native defect or zinc and copper. Since Zn_i has two excess electrons and Cu_{Zn} one deficit a $\text{Cu}_{\text{Zn}}\text{Zn}_i$ complex is expected to be a simple donor. This model is further discussed in Sec. IV.

The concentration profile can, however, also be explained by migration. At room temperature the donors are ionized and if they are sufficiently mobile they can migrate in the large electric field in the depletion

layer and pile up near the surface.

The identification as a donor is strongly supported by the large electron capture cross section σ_n which was found to be $>>10^{-15} \text{ cm}^2$ and too large to be measured with our equipment.

The thermal emission rate of electrons e_n^t was measured in the same way as for Cu_{Zn} . Also in this case deviations from exponentiality were observed but were found to be temperature independent. These are, at least partially, due to the extreme distribution of the center. An Arrhenius plot of e_n^t/T^2 is presented in Fig. 7. The slope corresponds to an energy of 0.293 eV. A straightforward DLTS measurement of e_n^t/T^2 in the temperature interval 160-200 K gave the considerably higher energy 0.362 eV.

Finally the photoionization cross section σ_n^0 was measured using photo-capacitance transient techniques^{23,24}. The diode was first zero-biased to fill the centers with electrons and then reverse biased. After thermal emission from Cu_{Zn} had faded out the diode was illuminated with monochromatic light from a Zeiss MM3 double prism monochromator and the resulting capacitance transient recorded. The procedure was repeated for different photon energies and the time constant of the transients evaluated as above. The photon flux of the monochromator was measured with a calibrated thermocouple. In Fig. 8 the spectrum of σ_n^0 is shown in a semilogarithmic scale. A number of peaks in the spectrum indicate the existence of both discrete excited states and resonances near the conduction band edge. The sharp peaks below 0.58 eV are probably due to discrete states and the broader ones at higher energy to resonances. A detailed classification can, however, hardly be based on the limited information available.

Since the temperature dependence of the electron capture cross section is not known an accurate determination of the energy position of this level could not be performed. The existence of excited states is a further complication in such a determination.

A PC spectrum resembling the spectrum of σ_n^0 (though no peaks are seen) has also been reported in some of the references on surface states cited above^{29,31}. Also in this case the assignment to surface states is questionable (see Sec. IV).

C/ The 0.16 eV level

At temperatures below 40 K a new PC band shows up on the low-energy side of the spectrum reported above. In Fig. 9 this spectrum at 8 K is shown (linear scale). The spectral behaviour is very irregular which probably is the combined effect of excited states and surface effects (see Sec. IV). Some structures interpreted as LO phonon replica of the features A-E have been marked in the figure. $\Delta = \hbar\omega_{LO} = 72$ meV. The steep rise at approximately 0.15 eV is interpreted as an ionization edge. Probable candidates for this band are the 0.165 eV native donor, assigned to the oxygen vacancy, or the second donor level of interstitial zinc³⁸. Surface states cannot be excluded. The level is too shallow to be observed in capacitance measurements why no thermal emission has been studied.

IV. Discussion

The absorption spectrum of Cu_{Zn} corresponding to optical electron emission (Fig. 5) indicates the existence of resonances in the conduction band. Photocapacitance measurements show that the absolute value of the photoionization cross section of electrons is extremely small, roughly 10^{-20} cm^2 . Since the acceptor ground state is of rather pure d-character¹ transitions to the predominantly s-like conduction band are not allowed, which is consistent with the small cross section. Any perturbation of the conduction band enhancing the small odd-parity content would relax the parity selection rule thereby increasing the transition probability. Also quasi-localized

states of even parity could relax the selection rule via coupling to odd-parity phonons. Such distortions of the continuum might be commonly occurring for deep centers but difficult to observe in the presence of strongly allowed transitions to the undistorted band states. When transitions to undistorted states are forbidden however, even weak distortions could have a profound effect on the corresponding ionization spectrum. We propose the latter case to be applicable to Cu_{Zn} .

The t_2 ground state level is split into three nearby levels by spin-orbit coupling and the trigonal lattice distortion in wurtzite structure, and the remaining hole can be left in any of these levels after photoionization. One single resonant level in the band thus would give rise to three nearby peaks in the ionization spectrum in the absence of phonon coupling. When this coupling is taken into account a complicated vibronic band is expected. One resonance thus could give rise to an absorption spectrum of the type observed. However, to explain the difference between the absorption and the PC spectrum at least one more resonant level is required. One level at lower energy is supposed to be the origin of the sharp absorption peaks in the 0.20-0.24 eV range. These are not seen in PC which we explain by fast deexcitation to the acceptor ground state and thus a small release rate to the conduction band. Another level at higher energy with a slower deexcitation is supposed to give rise to the main part of the photoconductivity in the 0.25-0.30 eV range and contribute to the absorption above 0.24 eV. Since the rate of deexcitation by multiphonon emission (see below) is strongly decreasing with increasing energy to be dissipated the assumption of much faster deexcitation from the lower resonance seems plausible.

In addition to the peaks the general shape of the absorption band also supports the assumption of a perturbed band since it indicates that transitions to states near the bottom of the band are more probable than transitions to higher states, resulting in a rather narrow band. A broad ab-

sorption band is expected for an unperturbed band since the acceptor ground state is strongly localized in real space and thus delocalized in k space.

The PC band also falls off in the 0.3-0.4 eV range but the influence of the surface (see below) and the assumed contribution from the deep donor make a discussion of the spectral shape difficult.

The existence of resonances requires a potential strongly distorting the conduction band continuum. Since Cu_{Zn} is neutral after electron emission no Coulomb interaction is present in the final state and only short-range interactions remain. Central-cell potentials at neutral impurities have been discussed in the literature in terms of electronegativity differences between impurity and host atoms. Local strain around a defect has also been suggested to act as an attractive potential, but neither this nor the electronegativity approach seems appropriate here. A more probable mechanism is final-state interaction between the excited nearly-free electron and the remaining hole in the Cu 3d-shell. Final-state interaction in photoionization has been observed and analyzed in the case of $\text{ZnSe}:\text{Co}^{40}$. The properties of the blue Co-emission and corresponding absorption, including magnetic field and stress dependence, are explained using a model of a loosely bound electron, derived from the symmetric conduction band minimum, interacting with the unfilled Co 3d-shell. In this case the center is positively charged after ionization and the excited electron is subject to Coulomb attraction. In addition to the Coulomb potential however, a strong central-cell potential affecting the loosely bound electron is deduced from the experimental data. We propose a similar short-range potential in the case of Cu_{Zn} giving rise to the resonances in the band. A detailed classification of the corresponding electron states is not easy to perform since no data on magnetic field or stress dependence are available and probably cannot be obtained because of the width of the peaks. A further complication is the Jahn-Teller interaction which results in an

intriguing phonon interaction³⁹.

In the case of the deep donor the situation is different since the photoionization cross section of electrons is of normal magnitude, 10^{-16} cm^2 , and transitions to the conduction band obviously allowed. The interesting spectral features, interpreted in terms of discrete excited states and resonances, are seen close to the continuum edge. The nature of these states is rather obscure since the center is not identified. After electron emission a simple donor, i.e. a donor with filled d-shell, holds no hole and only one-electron excited states are expected. If the Coulomb interaction dominates a Rydberg series would appear. The spectrum of σ_n^0 (Fig. 8) is not consistent with such a series however.

One suggestion is the presence of an unfilled d-shell also in this case. As mentioned above a $\text{Cu}_{\text{Zn}}\text{Zn}_i$ complex is a possible candidate for this center. In the simplest approximation the Cu part accepts one of the two excess electrons of the Zn part. However, this electron transfer cannot be expected to be complete since it would create a large electrostatic field opposing it. In the next order of approximation we therefore let the d-orbitals of the Cu part be partially occupied and the donor orbitals of the Zn part holding the rest of the charge. We write for the neutral center $\text{Cu}_{\text{Zn}}^{\delta-}\text{Zn}_i^{1-\delta-}$ and for the ionized (positive) center $\text{Cu}_{\text{Zn}}^{\gamma-}\text{Zn}_i^{2-\gamma-}$, where $0 < \delta_- < 1$ and $0 < \gamma_- < 1$. In excited states of the neutral center intermediate cases could occur. The partial occupancy is expected to cause strong hybridization between the d-orbitals and the donor orbitals which would result in a complicated electronic structure.

Besides these specific models presented to explain the excited states or resonances of Cu_{Zn} and the deep donor the recently developed Green's function scattering theoretic methods for deep centers predicts such states within a more general framework⁴¹⁻⁴³. When discussing these states in general it should also be noted that both resonances and phonon replica of discrete excited states can give rise to peaks as well as dips in the io-

zation spectrum as analyzed by Fano⁴⁴. Fano resonances have been observed in several ionization spectra in silicon⁴⁵⁻⁴⁷.

When studying thermal emission and capture excited states and resonances are of crucial importance. The temperature dependent transition rates for excitation and deexcitation between all pairs of discrete levels and between all discrete levels and the continuum, distorted by resonances, as well as the temperature dependent release rates from the resonances enters in the rate equations for the total emission or capture processes. Such equations have been discussed or solved in the literature for some simple cases^{14,33-35}. We do not attempt a detailed analysis here but note that the existence of excited states sufficiently deep that transitions to the continuum are thermally activated in general results in a total capture strongly decreasing with increasing temperature^{33,34,52}. According to the detailed balance equation³² this in turn results in an activation energy for emission considerably smaller than the true energy distance from the ground state to the continuum. We propose this mechanism to be the reason for the low activation energy for thermal electron emission from the deep donor.

We also note that the observed thermal emission rate of electrons for Cu_{Zn} is considerably larger than expected. Using thermodynamical arguments the emission rate can be related to the capture cross section, the optical ionization threshold and the activation energy of the emission via the detailed balance equation³². If our experimental data and the usual expression for the effective density of states in the conduction band are used, an emission rate roughly 60 times smaller than the one observed is calculated. This discrepancy might be due to distortions of the band. Electric field enhancement of the emission cannot be excluded however, since emission is measured in the strong field of the diode depletion layer while capture is measured in a field free region.

The capture of free carriers by deep centers are, at moderate carrier densities, generally believed to be either radiative or caused by multiphonon (MP) emission. Radiative capture is in principle temperature independent while MP capture is thermally activated for temperatures such that $kT \approx \hbar\omega$, where $\hbar\omega$ is the energy of the phonons involved, and temperature independent if $kT \ll \hbar\omega$. In the latter case tunneling through the vibronic barrier dominates. A general analysis of MP capture is rather involved and simplifications are often made to obtain analytical expressions of the capture rate⁴⁸⁻⁵¹.

Since the probability of radiative capture strongly decreases with decreasing depth E_T of the ground state level while the probability of MP capture strongly increases the latter is assumed to be the most important for Cu_{Zn} . However, the simplified calculations of MP capture generally assume $E_T \gg \hbar\omega$. In the case of Cu_{Zn} $E_T \approx 0.17$ eV while the phonon energies in ZnO are rather large, $\hbar\omega_{\text{LO}} = 72$ meV, and the condition $E_T \gg \hbar\omega$ is not valid. A fit of our data to such calculations are thus probably of a limited value. The thermal activation observed is, however, in general agreement with these models.

As mentioned earlier PC spectra similar to the PC and photocapacitance spectra in this paper have been reported and assigned to surface states²⁹⁻³¹. There are several reasons to doubt this assignment:

- 1) The capacitance transients and optical absorption reported here are true bulk effects. The two defects studied have approximately the same photoionization thresholds as the two main PC bands attributed to surface states²¹.
- 2) These two PC bands seem to be relatively stable against varying surface pretreatment and are seen on both prism and polar faces in spite of the different structure of these²¹. The somewhat different spectral shapes are discussed below.

3) A model recently proposed by Heiland and Kohl clearly demonstrates that a number of surface effects, among them surface PC, can be caused by bulk defects within an accumulation layer close to the surface⁵³. Sensitivity to surface treatment is easily explained by true surface states changing the Fermi level.

The crystals used for electrical measurements contain Al donors ($N_D = 10^{16}$ - 10^{17} cm⁻³, $E_D \approx 30$ meV) which together with Cu_{Zn} and the deep donor give a set of energy levels very similar to one (of two) used in the model of Heiland and Kohl. If the 0.16 eV native donor is included we have a set very similar to the second one used in the model.

The PC measurements reported here were performed in vacuum where oxygen leaves the surface (before cooling) and makes an accumulation layer possible.

The interpretation in ref. 30 of the periodic minima in the PC spectrum (marked with arrows in Fig. 3) as being due to recombination assisted by bulk and surface phonons is still valid within the model of Heiland and Kohl. The current is mainly flowing very close to the surface and the recombination thus governed by true surface states or bulk processes close to the surface. Surface phonons are therefore expected to show up in the spectrum. Note that the analysis in ref. 30 yields the value 0.17 eV for the zero-phonon threshold.

The overall shape of the spectrum in Fig. 3 and the one reported in ref. 30 is slightly different which is a natural consequence of the model since the different crystals cannot possibly have identical surface properties. Different surface recombination also could explain the somewhat different spectral behaviour of prism and polar faces in addition to the fact that true surface states seem to contribute to the PC on polar faces. It also could explain part of the difference between the PC and absorption spectra reported here, especially in the 0.3-0.4 eV range. The differences around 0.2 eV are probably due to fast deexcitation from resonant states

and to different selection rules as discussed in Sec. III.

The irregular shape of the low-energy PC band (Fig. 9) also might be explained by the combined effects of excited states and phonon interaction. In this case phonon assisted excitation seems to be more important than phonon assisted recombination since LO phonons give rise to peaks (marked in Fig. 9) instead of dips.

Finally it should be mentioned that detectable amounts of copper almost always seem to be present in II-VI compounds unless specific purification procedures have been employed. Therefore Cu-related centers often are observed even in nominally undoped material.

V. Conclusions

The extension of capacitance spectroscopy to II-VI compounds have made possible the study of thermal electron emission and electron capture for the Cu_{Zn} acceptor in ZnO , which is found to have a ground state level approximately 0.17 eV below the conduction band. This small energy makes a conventional photocapacitance measurement difficult to perform. Therefore Fourier transform spectroscopy was employed to study photoconductivity and optical absorption ascribed to optical electron emission from this center. The absorption spectra exhibit pronounced structure which is interpreted in terms of resonances in the conduction band due to final-state interaction between the excited electron and the remaining hole in the Cu 3d-shell. A small transition probability to undistorted s-like band states is assumed to make these resonances dominant in absorption. The photoconductivity spectrum is assumed to be modified by surface effects since the current is believed to flow mainly within an accumulation layer close to the surface. Earlier photoconductivity spectra attributed to surface states are discussed in this context.

A deep donor has also been found and capacitance spectroscopy has been used to measure thermal and optical electron emission. The electron capture cross section was found to be too large to be measured. The concentration of the donor rises dramatically close to the surface which might indicate a relation to excess zinc. The photoionization cross section of electrons also exhibits a pronounced structure, indicating the existence of discrete excited states and resonances near the conduction band edge. The nature of these is rather obscure since the center is not identified but a model of a $\text{Cu}_{\text{Zn}}\text{Zn}_i$ complex with hybridized d- and donor orbitals is suggested.

At low temperatures a low-energy photoconductivity band appears. The spectrum is very irregular which is interpreted as the combined action of excited states and surface effects. An ionization edge at about 0.15 eV makes the 0.165 eV native donor or the second donor state of Zn_i probable origins of this band.

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Figure captions

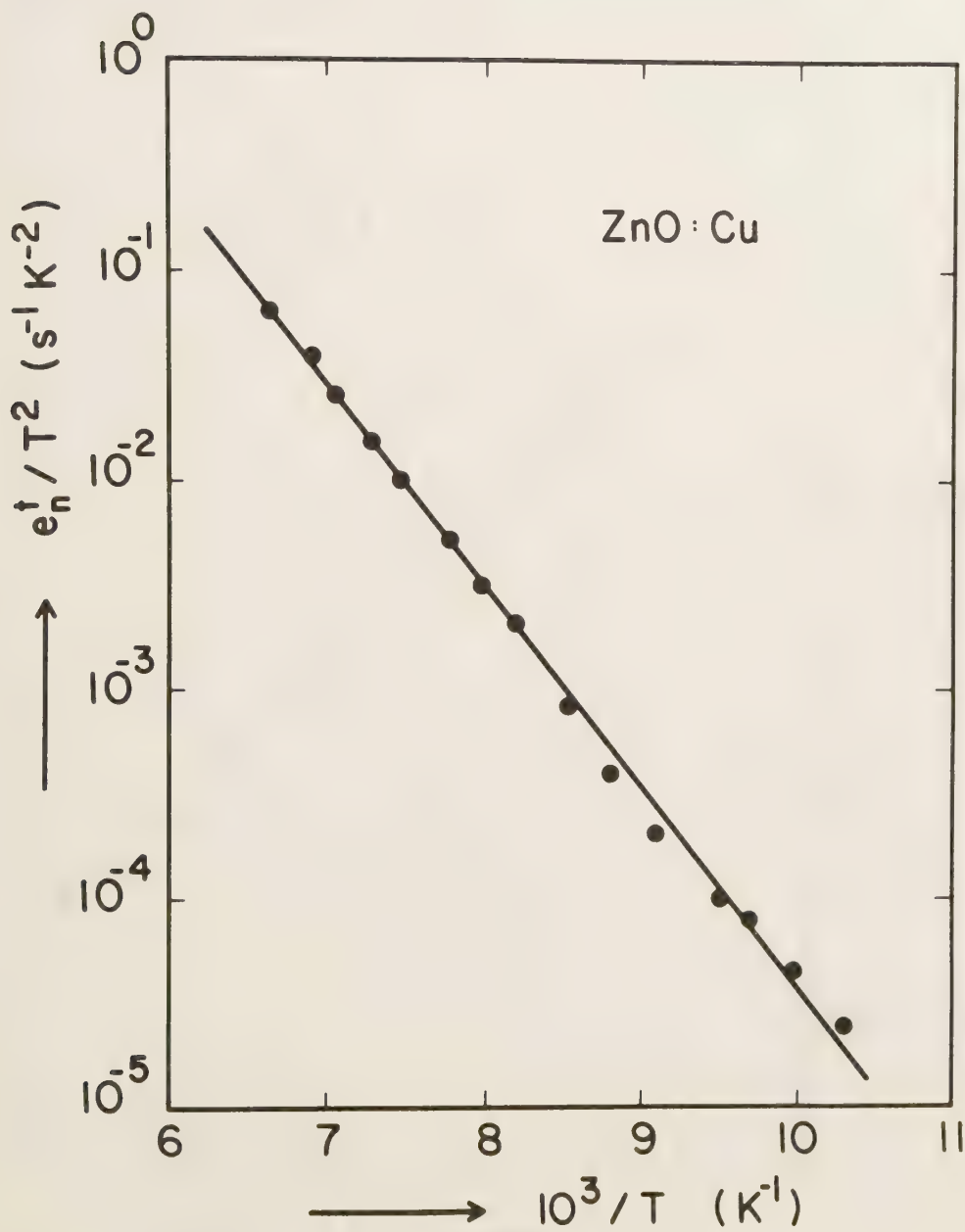
- Fig. 1 Arrhenius plot of e_n^t/T^2 for Cu_{Zn} . The slope corresponds to an energy of 0.193 eV.
- Fig. 2 Arrhenius plot of the electron capture cross section σ_n for Cu_{Zn} . The slope corresponds to an energy of 28 meV.
- Fig. 3 Photoconductivity spectrum at 65 K, linear scale. The arrows corresponds to those in ref. 30.
- Fig. 4 Photoconductivity spectrum at 65 K, semilogarithmic scale.
- Fig. 5 Absorption spectrum at 8 K (upper curve) and 78 K (lower curve). Light incident parallelly to the crystal c-axis.
- Fig. 6 C-V characteristics of a diode where the deep donors in the depletion region are a) filled with electrons, 129 K, and b) empty, 145 K. The deviation due to the deep donor is marked with an arrow.

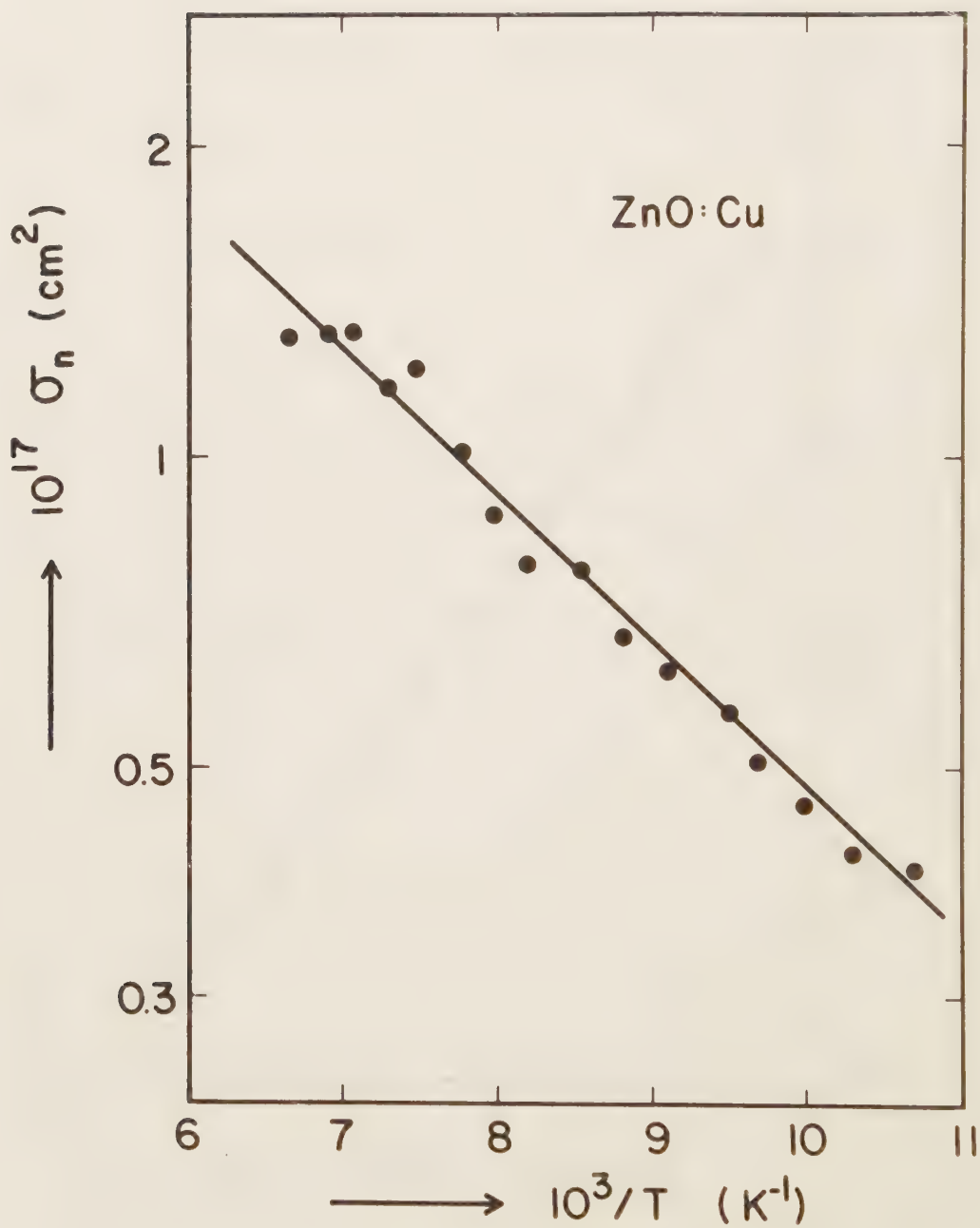
Fig. 7 Arrhenius plot of e_n^t/T^2 for the deep donor. The slope corresponds to an energy of 0.293 eV.

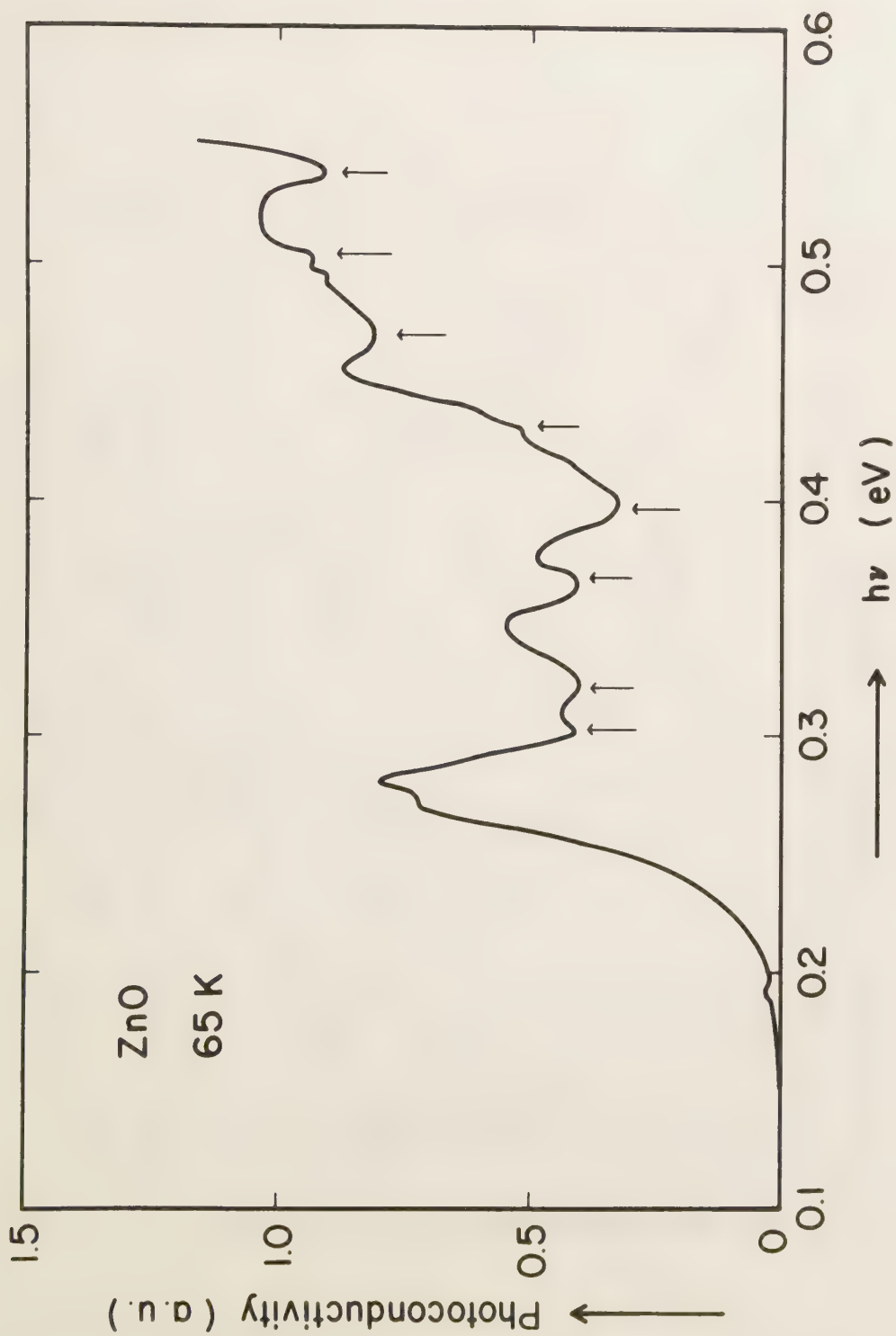
Fig. 8 Photoionization cross section of electrons σ_n^0 for the deep donor, semilogarithmic scale.

Fig. 9 Photoconductivity spectrum at 8 K, linear scale. $\Delta = \hbar\omega_{LO} = 72$ meV.

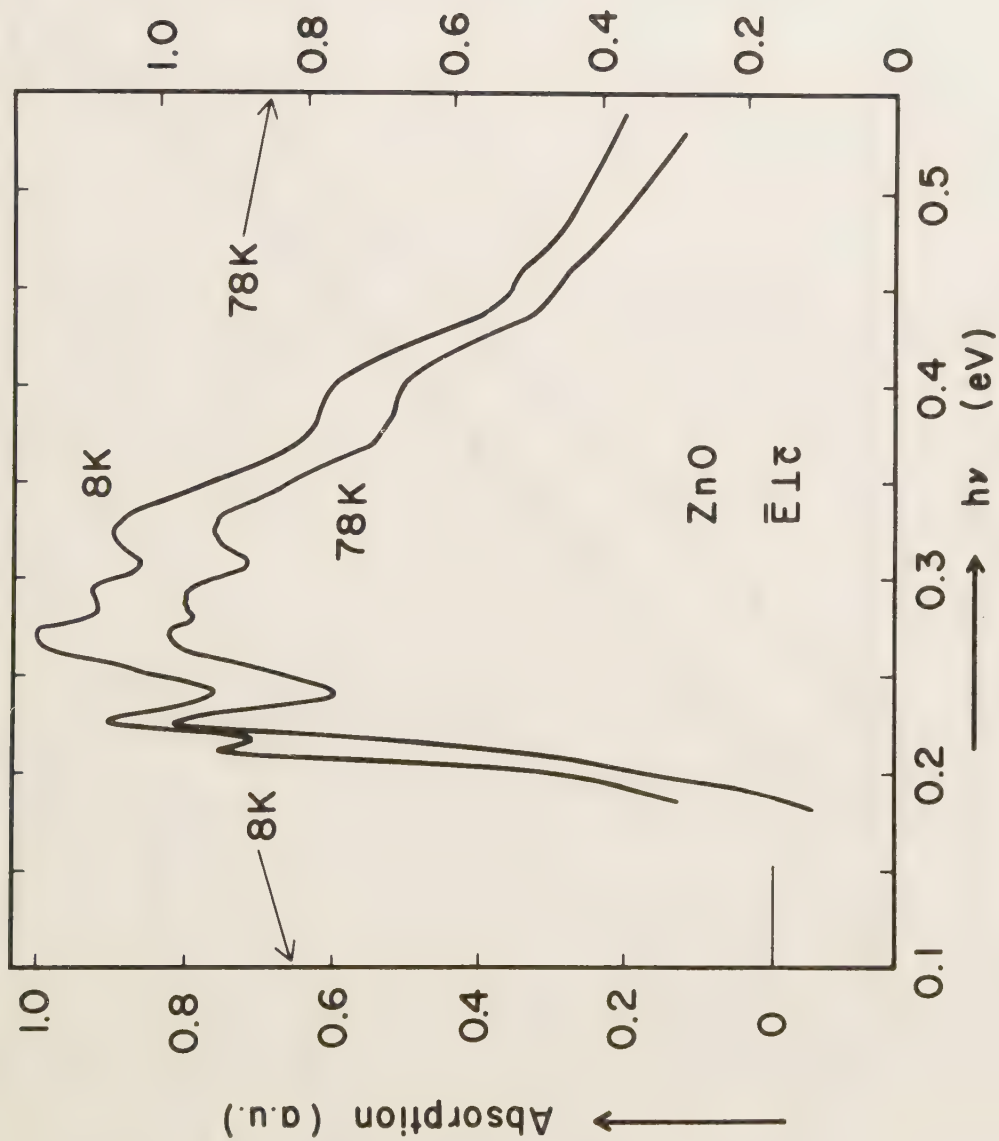
Fig. 10 Summary of the energy levels discussed in this paper. t_2 and e are the one-hole Cu d-levels split apart by the T_d field. CT are the one-hole Cu charge-transfer states giving rise to the "Cu-green" emission. DD is the deep donor level and ND the native 0.165 eV donor level. Al is the aluminum donor level and Zn_i the interstitial zinc donor level. CB is the conduction and VB the valence band edge of ZnO.

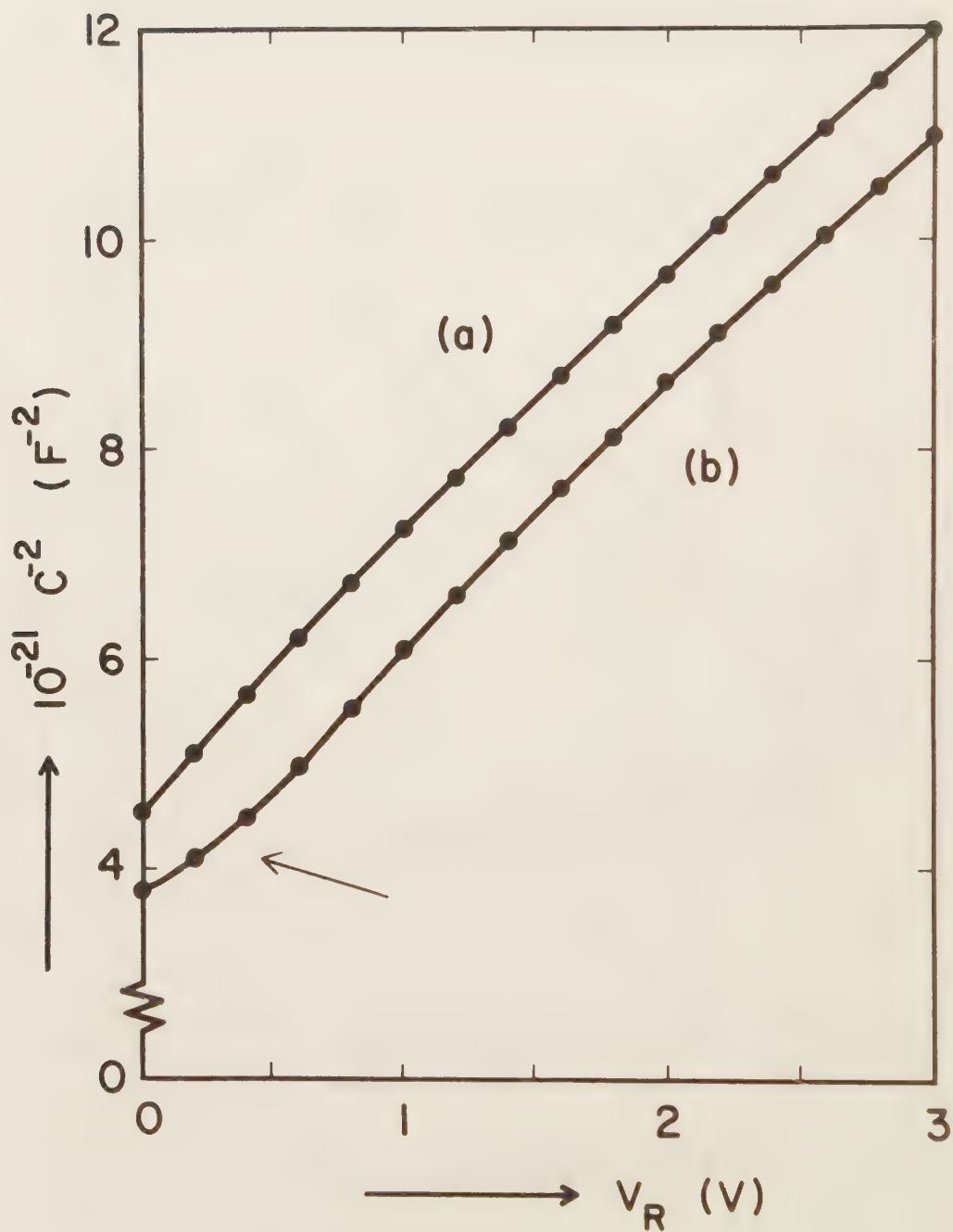


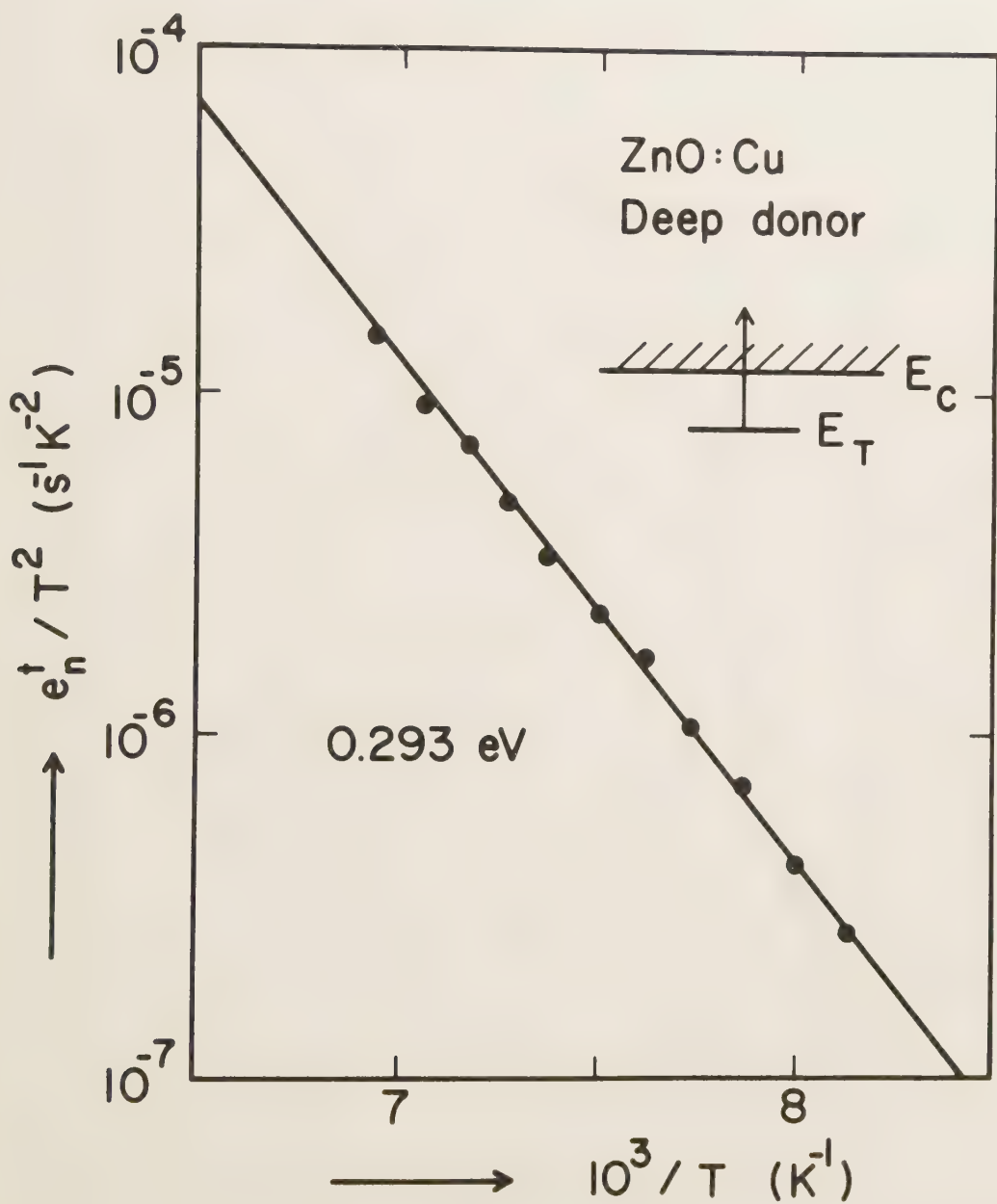


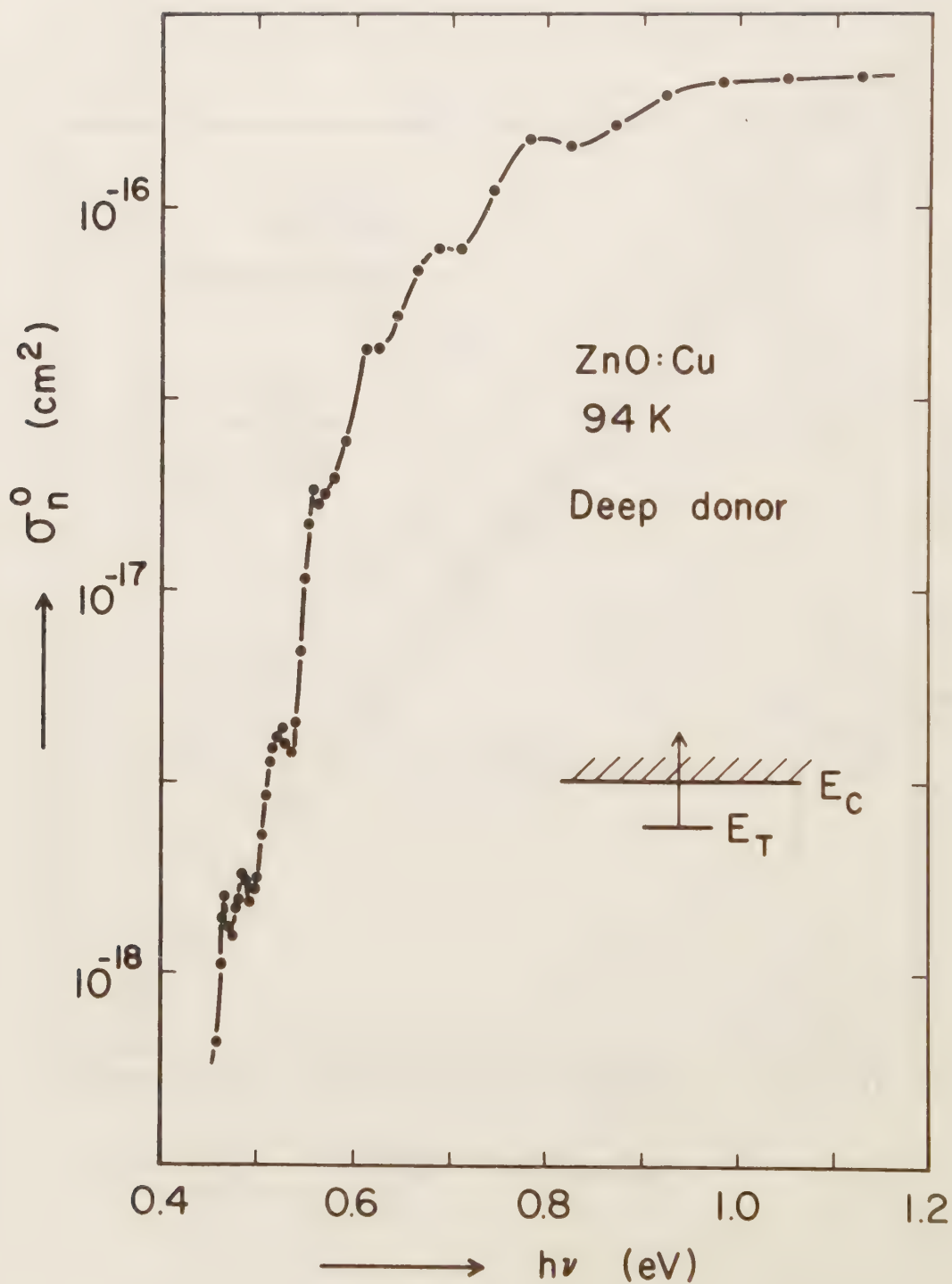


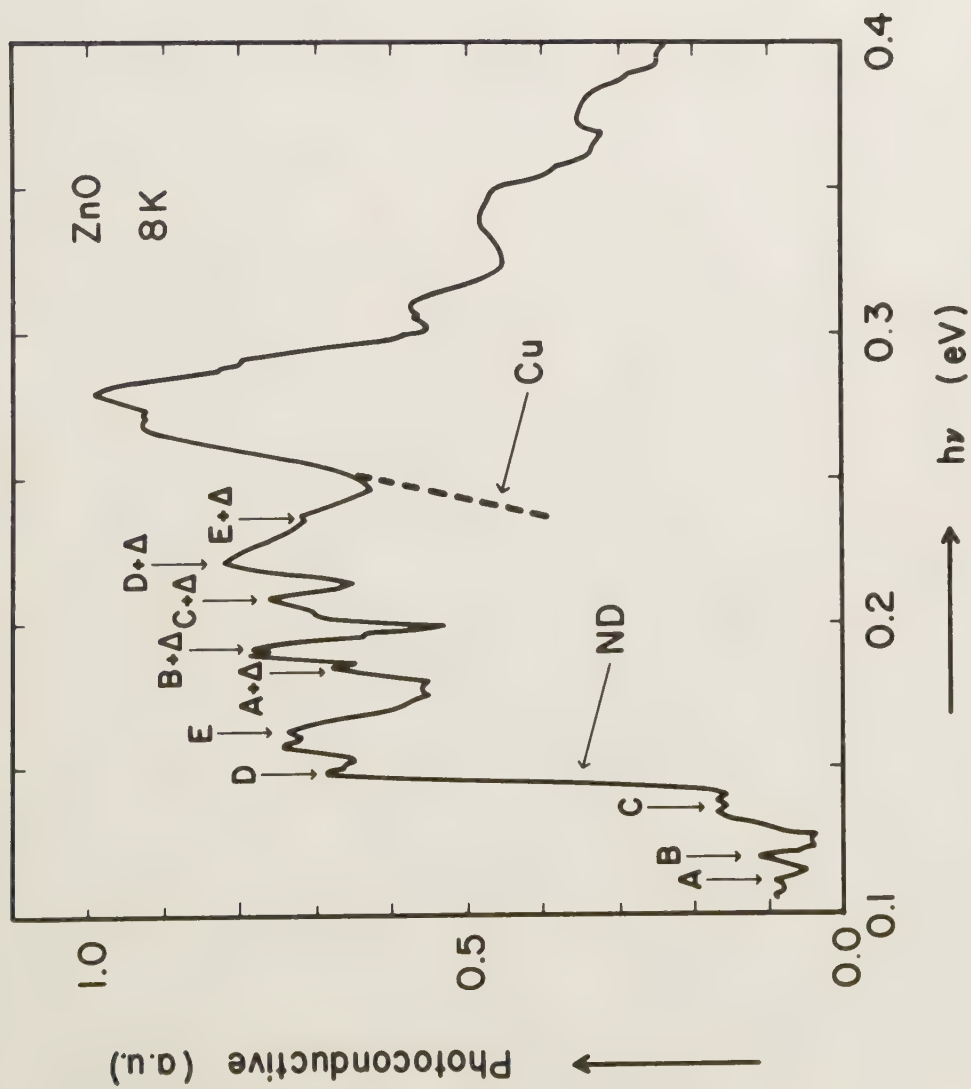


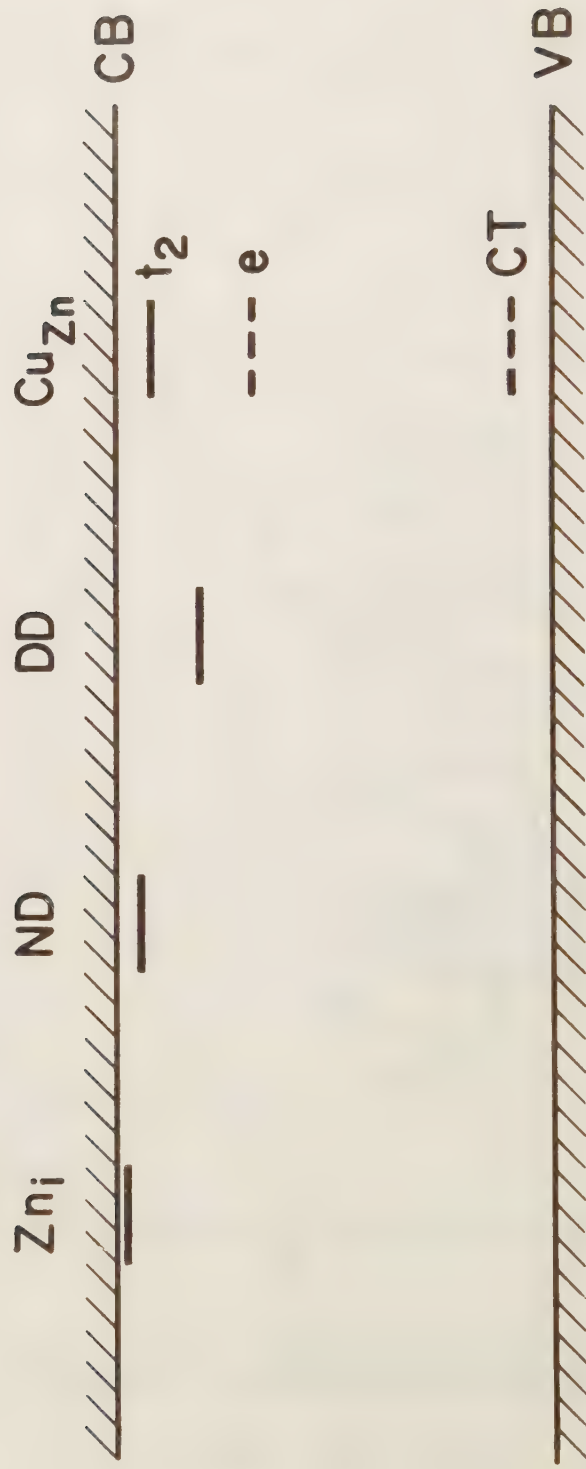












PROPERTIES OF COPPER RELATED DEEP CENTERS IN III-V SEMICONDUCTORS

N. Kullendorff, L. Jansson, and L.-Å. Ledebö*

Department of Solid State Physics, University of Lund, Box 725,
S-220 07 LUND, Sweden

*Present address:

Innovance AB, Magle St. Kyrkog. 8, S-223 50 LUND, Sweden

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Abstract

Copper diffused InP and GaAs have been studied using junction space charge spectroscopy. Two dominant copper related deep levels are observed in both materials. Photoionization cross sections of holes and electrons, thermal hole emission rates, and one electron capture cross section have been measured. In InP one of the ionization spectra exhibits a pronounced phonon related structure.

The results, together with previous work on GaAs:Cu, GaP:Cu, GaAsP:Cu and AlGaAs:Cu, show that the two dominant levels have approximately the same positions relative to the vacuum level in all the materials and give a coherent picture of the role of copper related deep levels in III-V compounds.

I. Introduction

Copper is one of the most frequent impurities in III-V compounds. It diffuses rapidly even at comparatively low temperatures and is therefore commonly occurring in these materials where it gives rise to both radiative

and non-radiative recombination centers. In spite of extensive work on Cu in III-V compounds, including studies of luminescence¹⁻¹², photoconductivity¹³⁻¹⁵, Hall effect^{1,16-18} and junction measurements^{14,19,20} no coherent picture of the role of Cu in these materials has been presented. By studying Cu diffused InP and GaAs using junction space charge techniques and comparing the results with published work on GaAs:Cu and GaP:Cu as well as recent results on AlGaAs:Cu and GaAsP:Cu we have been able to outline a unified description of Cu-related deep levels in III-V semiconductors which is presented and discussed in Sec. IV.

The results on InP:Cu are also of great interest in themselves since, to our knowledge, no work on this system has been reported and since a pronounced structure has been found in one of the ionization spectra. This structure is discussed in Sec. IV in terms of Fano resonances due to LO phonon replica of transitions to excited states close to the valence band edge. A similar but weaker structure is seen in published spectra for GaAs:Cu. In InP additional structure at an energy corresponding to the spin-orbit splitting of the valence band is observed.

The results on InP:Cu are also of interest as a data point for Cu in ternary and quarternary alloys between InP and other III-Vs. These alloys have attracted intense interest during recent years since they provide the active material in semiconductor lasers and LEDs operating at 1.3 and 1.6 μm and thus are of decisive importance for optical communication technology. Deep centers in semiconductor alloys are also of scientific interest since the composition dependence of the deep level properties gives new insight in both the nature of the centers themselves and the band structure of the host material.

II. Sample preparation

A/ InP

Samples were prepared from a polished (100) slice of commercial InP grown by the liquid encapsulation Czochralsky (LEC) technique. The slice was nominally undoped and had a free electron concentration of $4 \cdot 10^{14} \text{ cm}^{-3}$. p^+n -junctions were prepared by Zn diffusion in an evacuated quartz ampoule (volume approximately 3 cm^3). The diffusion source was 1 mg of red ZnP_2 , prepared from Zn of purity 5N and analysis grade phosphorous. A diffusion at 680°C for 15 min resulted in a $7 \mu\text{m}$ deep p region. 50 nm of Cu was then evaporated onto part of the slice, followed by a diffusion at typically 600°C for 2 h. Crushed InP was present in the ampoule to establish an equilibrium phosphorous pressure. In no part of the process did we observe surface degradation due to phosphorous losses. After sand blasting of the back side to remove the p layer ohmic contacts were evaporated. The p and n contacts were made by evaporation of a Zn/Au/Cr and Sn/Au/Cr sequence respectively. Contact alloying was made at 500°C for half a minute. Reference samples and copper diffused samples were subject to identical processing with the exception of Cu evaporation. The slices were cleaved in $0.3 \times 0.3 \text{ mm}^2$ dice, mounted with silver epoxy on T0-5 headers and ultrasonically bonded.

The concentration of the two dominant Cu-related deep levels, Cu_A and Cu_B , could be conveniently monitored using DLTS and their diffusion behaviour thus easily studied. Cu_A is the level closest to the valence band (see Sec. III). The results are summarized in Tab. 1. The data show that Cu_A is more abundant than Cu_B for all diffusions and thus more easily introduced in the material than Cu_B .

Diffusion at higher temperature, 625°C (2 h), or of longer duration, 20 h (575°C), resulted in two additional levels 0.3-0.4 eV above

the valence band. Their concentrations were of the order of 10^{12} cm^{-3} in both cases. These levels are discussed in Sec. IV.

In the reference samples no other deep level than Cu_A could be detected at a detection limit of approximately $1 \cdot 10^{11} \text{ cm}^{-3}$. The reference samples were thus very pure, in contrast to samples processed according to McAfee et al²² who, normally using Zn_3P_2 and excess phosphorous as diffusion sources, found approximately 10^{14} cm^{-3} deep level impurities in the upper half of the band gap.

B/ GaAs

Samples were fabricated using the liquid phase epitaxy (LPE) technique. Most of the measurements were performed on n^+p -junctions, made by growing a Sn doped n^+ -layer ($n=10^{18} \text{ cm}^{-3}$) and a Ge doped p -layer ($p=5 \cdot 10^{15} \text{ cm}^{-3}$) on top of an n^+ -substrate. 50 nm of Cu was evaporated onto the p -layer, followed by a diffusion at 625°C for 2-20 h in an evacuated quartz ampoule. Reference samples were subject to identical processing (except for Cu evaporation). The final fabrication steps - contacting, cleaving and mounting - were made in the same manner as for the InP samples.

For some measurements p^+n -junctions and n -Schottky barriers were employed. In both cases LPE was used to grow an n -layer on the n^+ -substrate. The p^+ -layer of the p^+n -junction was made by Zn diffusion at 710°C for 5 min. Cu diffusion was performed as described above in both cases. The Schottky barrier was made by finally evaporating 10 nm of Cr onto the n -layer.

The concentration of deep levels in the Cu diffused samples was approximately 10^{14} cm^{-3} and several orders of magnitude larger than in the reference samples.

III. Experimental results

A/ Thermal emission rates of holes

The thermal emission rate of holes e_p^t was measured using the standard DLTS technique²¹ complemented with single-shot capacitance transients^{23,24} to expand the rate window. The DLTS set-up used for this work is described in ref. 25. The single-shot measurements and the measurements of photoionization and low-temperature capture cross sections presented in Sec. III B and C were performed using a Boonton 72 BD capacitance meter and a Leybold-Heraeus gas flow cryostat. In the case of GaAs:Cu_A admittance spectroscopy²⁶ was employed since this level is too close to the valence band to be conveniently studied by standard DLTS. The admittance was measured with an Ortoloc-SC two phase lock-in analyser.

For the study of the InP:Cu_A center diodes with a concentration of $1.5 \cdot 10^{13} \text{ cm}^{-3}$ of this center and a negligible concentration of other centers were used. An Arrhenius plot of e_p^t divided by T^2 is presented in Fig. 1. The slope corresponds to an energy of 0.26 eV. A fit to the DLTS data only gives the energy 0.27 eV. The same energy is found for the dominant hole trap in nominally undoped InP^{22,27}.

When studying the InP:Cu_B center diodes with a concentration of $6 \cdot 10^{11} \text{ cm}^{-3}$ of this center were used. An Arrhenius plot of e_p^t/T^2 is shown in Fig. 2. The slope corresponds to an energy of 0.64 eV. The same energy is reported for the second most abundant hole trap in nominally undoped material²².

An Arrhenius plot of the admittance peak frequency f_p divided by T^2 for GaAs:Cu_A is shown in Fig. 3. The slope corresponds to an energy of 0.13 eV, in approximate agreement with Hall effect data^{16,17}. In Fig. 4, finally, an Arrhenius plot of e_p^t/T^2 for GaAs:Cu_B is presented. The slope corresponds to an energy of 0.40 eV. A fit to the DLTS data only gives the energy 0.44 eV, in agreement with published DLTS results¹⁹.

B/ Photoionization cross sections

Photoionization cross sections of holes and electrons were measured using photocapacitance transient techniques^{23,24}. A Zeiss MM3 or MM12 double prism monochromator was used as primary light source and a Bausch&Lomb grating monochromator was used as high-intensity source. The photon flux ϕ of the primary light source was monitored using a calibrated thermocouple. The same samples were used as for the thermal emission measurements with a few exceptions mentioned below. In all optical experiments reverse bias was applied to the diodes to decrease the influence of the free carrier tails²⁸.

In the case of InP:Cu_A a modified version of the steady-state constant capacitance method²⁹ permitted a higher resolution than transient techniques when measuring the photoionization cross section of holes σ_p^0 , provided that samples with a high concentration ($3 \cdot 10^{14} \text{ cm}^{-3}$) of this center were used. This modified version is described in Appendix.

The photoionization cross section of holes σ_p^0 at 78 K for InP:Cu_A is presented in Fig. 5 in a semilogarithmic scale and is drawn as a continuous curve since it is measured for more than 120 photon energies. Pronounced structure is seen in the spectrum and the dips are marked with arrows in the figure. The structure is discussed in Sec. IV.

Efficient excitation of electrons from the InP:Cu_A level into the conduction band is difficult to achieve due to its small energy distance from the valence band. Therefore a measurement of the photoionization cross section of electrons σ_n^0 could not be performed.

The photoionization cross section of holes σ_p^0 for InP:Cu_B was measured as follows. Initial non-zero hole occupancy was established by using high-intensity light of 1.0 eV photon energy, which is sufficient to excite electrons from this level into the conduction band. This light was

then replaced by low-energy light, $h\nu < 0.85$ eV, which excites the bound holes into the valence band, thus giving rise to a capacitance transient whose inverse time constant is equal to the product of σ_p^0 and ϕ ^{23,24}. The spectrum of σ_p^0 at 112 and 171 K is shown in Fig. 6. No structure can be seen in this spectrum. The threshold energy for photoionization is somewhat obscured by phonon broadening and possibly electric-field broadening but is estimated to be approximately 0.55 eV. This energy is considerably smaller than the corresponding thermal activation energy 0.64 eV. This is discussed in Sec. IV.

The photoionization cross section of electrons σ_n^0 for InP:Cu_B was measured in a similar manner. Initial zero hole occupancy was established by using high-intensity light of 0.76 eV photon energy, which excites all bound holes into the valence band. This light was then replaced by low-intensity high-energy light, $h\nu > 0.78$ eV, which is sufficient to excite electrons from this level into the conduction band, i.e. two-step excitation results. In this case σ_n^0 is obtained from $\Delta C/\tau$ where ΔC is the magnitude and τ the time constant of the transient induced by the high-energy light^{23,24}. The spectrum of σ_n^0 at 112 and 171 K is shown in Fig. 7. This spectrum is also structureless. The threshold energy of σ_n^0 is, like for σ_p^0 , obscured by broadening but is estimated to be about 0.82 eV. The sum of the thresholds of σ_p^0 and σ_n^0 is approximately equal to the band gap of InP.

To estimate the absolute value of σ_n^0 we assume that the magnitude of σ_p^0 is approximately the same at 0.76 and 1.0 eV and use the relation $\tau/\phi = \sigma_p^0 + \sigma_n^0$ which is valid when two-step excitation occurs^{23, 24}.

The GaAs:Cu_A level is too close to the valence band to allow a conventional photocapacitance measurement of σ_p^0 . Optical absorption corresponding to σ_p^0 has been reported however^{30,31} and reveals an ionization threshold at 0.156 eV. In Fig. 8 the spectra from ref. 30 and 31 are shown. Fine structure caused by excited states are seen below the conti-

num and broad bumps, attributed to phonon assisted ionization, are seen at higher energies. Since GaAs:Cu_A is close to the valence band σ_n^0 cannot be measured, as was explained for InP:Cu_A.

The availability of n⁺p diodes simplified the measurements of σ_p^0 for GaAs:Cu_B. An initial zero voltage pulse fills the centers with holes. Subsequent illumination at reverse bias with light of photon energy smaller than 1.1 eV excites the bound holes into the valence band resulting in a capacitance transient. The σ_p^0 spectrum at 60 K is presented in Fig. 9. The threshold energy is approximately 0.40 eV, in agreement with the thermal data.

By using n-Schottky barriers σ_n^0 for GaAs:Cu_B was measured in a similar way. An initial zero voltage pulse fills the Cu_B centers with electrons. Subsequent illumination at reverse bias with light of photon energy larger than 1.07 eV results in two-step excitation. σ_n^0 is obtained from $\Delta C/\tau$ and was in this case evaluated by measuring the initial slope of the transients. The σ_n^0 spectrum at 60 K is shown in Fig. 10. The ionization threshold is about 1.07 eV. Thus the thresholds of σ_p^0 and σ_n^0 approximately add up to the band gap of GaAs. The absolute value of σ_n^0 was estimated in a similar way as for InP:Cu_B.

C/ Capture cross sections

The electron capture cross section σ_n was measured for InP:Cu_A using DLTS at higher temperatures and the pulse-train technique³² at lower temperatures. In the first case an injection pulse was followed by a majority carrier pulse of varying duration. The magnitude of the subsequent emission transient was measured as a function of majority carrier pulse duration. In the latter case an injection pulse was followed by a train of

majority carrier pulses and the resulting capacitance changes recorded. In both cases care was taken to decrease the influence of the free carrier tails²⁸.

An Arrhenius plot of σ_n for InP:Cu_A is presented in Fig. 11. The values for $T > 100$ K are obtained by DLTS while the low-temperature values are obtained by the pulse-train technique. The cross section is small, $6 \cdot 10^{-20}$ cm² at 120 K, and has a weak temperature dependence.

Approximate calculations of the hole capture cross section σ_p for InP:Cu_A and InP:Cu_B using the detailed balance equation³³ and the thermal emission data give the values $1.3 \cdot 10^{-13}$ cm² respectively $6 \cdot 10^{-15}$ cm². The former value is in agreement with the value calculated in ref. 27 for the dominant hole trap.

In ref. 19 DLTS measurements of both the hole and the electron capture cross section for GaAs:Cu_B are reported. The hole capture cross section σ_p has a value of $3 \cdot 10^{-14}$ cm² at 300 K and is slowly decreasing with increasing temperature while the electron capture cross section σ_n has the value $8 \cdot 10^{-21}$ cm² at 250 K and exhibits a weak temperature dependence.

IV. Discussion

A plot of the Cu_A and Cu_B levels in InP and GaAs on an absolute energy scale, i.e. relative to the vacuum level, together with the two dominant Cu-related deep levels in GaP^{10-15,20}, here denoted GaP:Cu_A and GaP:Cu_B, is presented in Fig. 12. The vacuum levels are obtained from ref. 34 and 35. The plot reveals a striking similarity between the three materials leading us to propose a close similarity between the Cu_A centers in the different materials and analogously for Cu_B, i.e. both Cu_A and Cu_B are

assumed to retain their respective geometrical structures when passing from one material to another. This proposal is strongly supported by recent results on $\text{Al}_x\text{Ga}_{1-x}\text{As}:\text{Cu}$ ³⁶ and $\text{GaAs}_{1-x}\text{P}_x:\text{Cu}$ ³⁷. In $\text{Al}_x\text{Ga}_{1-x}\text{As}$ both Cu_A and Cu_B were studied over the entire composition range. The results show that both levels move continuously with x relative to the valence band and keep their mutual energy distance, thus indicating a similar nature of Cu_A respectively Cu_B in GaAs and AlAs. In $\text{GaAs}_{1-x}\text{P}_x$ the Cu_B level was studied all over the composition range and was found to move continuously with x relative to the valence band, giving strong evidence for the similar nature of Cu_B in GaAs and GaP.

Even though a similar nature of the Cu_A centers is suggested, the varying distance to the valence band in the different materials is supposed to have a profound effect on the acceptor ground state wave function. In GaAs this wavefunction is assumed to be to a large extent composed of valence band states and rather delocalized while in GaP the wave function is assumed to be strongly localized. This implies a weaker respectively stronger phonon coupling in transitions from the conduction band or shallow donors which might explain the different shapes of the emission bands attributed to these centers^{1,11}.

The case of Cu in II-VI compounds is instructive in this context³⁸. $\text{ZnTe}:\text{Cu}_{\text{Zn}}$ is a comparatively shallow acceptor showing moderate phonon coupling in donor-acceptor pair emission³⁹ while $\text{ZnS}:\text{Cu}_{\text{Zn}}$ is very deep and gives rise to a strongly phonon-broadened donor-acceptor pair emission band.

Further results support the assumption of closely related centers in the different III-Vs. The distance between the equally-spaced dips in the σ_p^0 spectrum of $\text{InP}:\text{Cu}_A$ is equal to the LO phonon energy 42.8 meV, leading to the possible interpretation of these as Fano resonance dips due to LO phonon replica of discrete electronic transitions⁴¹. The dip expected at

0.43 eV is assumed to be obscured by additional structure discussed below. Fano resonances have been reported for several ionization spectra in silicon⁴²⁻⁴⁴. In our case the electronic transitions are assumed to take place between the acceptor ground state and excited Coulombic effective-mass type states close to the valence band top. Such states have been observed for GaAs:Cu_A³⁰. If the midpoint of the resonances is supposed to be 5-10 meV below the dip this interpretation locates the ionization edge at 0.31 eV since the excited states are 5-15 meV above the valence band top in InP⁴⁵. Unfortunately the measurements of σ_p^0 could not be performed below the ionization edge where the excited states are expected to show up.

The energy resolution of the measurement presented in Fig. 5 is not sufficient to reveal the detailed shape of the features of the spectrum and further work is needed to determine this shape. If the hypothesis of Fano resonances is correct the steep rise of the spectrum in the region 0.3-0.45 eV would distort the shape of the resonances and move the dip to slightly lower energies. This is indeed observed since the dips at 0.36 and 0.40 meV are displaced a few meV to lower energies relative to the series of dips at higher energy equally spaced by the L0 phonon energy.

A second ionization edge is expected at 0.42 eV since the spin-orbit splitting of the valence band of InP is 0.11 eV. Indeed a very steep rise is seen at 0.43-0.44 eV which we ascribe to the split-off band. This rise probably obscures the third phonon replicum expected at 0.43 eV.

A close inspection of the corresponding spectrum of GaAs:Cu_A reveals a similar but less pronounced structure³¹. In ref. 31 the bumps in the continuum are assigned to ionization with simultaneous L0 phonon generation. Such bumps are usually not seen in photoionization spectra however, and in view of our results on InP the interpretation given above seems plausible also in the case of GaAs:Cu_A. Note that the width of the dips is approximately the same, 10-15 meV, in both materials. Fig. 5 and 8 show that the phonon coupling is smaller in GaAs than in InP which is explained by the

much smaller depth of the acceptor and corresponding larger delocalization of the ground state wave function in the former case.

Another mechanism giving rise to phonon related dips in ionization spectra is hot carrier scattering by LO phonons enhancing the recombination⁴⁶. Since our measurements utilize pn-junctions where the photo-released holes are immediately swept out of the depletion layer recombination is supposed to have no effect on the ionization spectra. The spectrum of GaAs:Cu_A in ref. 30 and 31 is obtained from bulk material however, and the effect can not be excluded in this case.

The structured ionization spectra indicate a similar nature of the Cu_A centers in InP and GaAs. In the case of Cu_B no structure is seen. A peculiar feature of Cu_B in InP however, is the large activation energy for thermal hole emission, 0.64 eV, compared with the optical ionization energy of approximately 0.55 eV. If the high-temperature activation energy 0.44 eV for GaAs:Cu_B is compared with the optical energy 0.40 eV, a similar discrepancy is found. This activation energy is obtained for $T > 180$ K. For InP:Cu_B all thermal data are obtained for $T > 220$ K. These results might indicate a similar shift for both centers at higher temperatures. Such shifts have been observed for GaAs:Fe⁴⁷ and the "B" level in GaAs⁴⁸.

The thermal energy should be corrected for the temperature dependence of the hole capture cross section to obtain the ionization energy since this cross section enters in the detailed balance equation³³. However, for GaAs:Cu_B this cross section is weakly decreasing with increasing temperature¹⁹ and such a correction makes the discrepancy even larger. No information on the temperature dependence of the hole capture cross section of InP:Cu_B is available, but the results on GaAs:Cu_B and the trends proposed above make the assumption of a thermally activated capture process less probable.

The reason for this shift is not clear. One possibility could be a thermally activated hole capture in the presence of an electric field. Emission is measured in the strong field in the depletion layer of a diode whereas

capture is measured in a field-free region. If the temperature dependence of the capture mechanism changes from a weak dependence without electric field to thermal activation in a large field this could explain our results. Another possibility could be the existence of resonances (and antiresonances) in the valence band distorting the density of states thereby violating the usual assumption of a $T^{3/2}$ dependence of the effective density of states N_V which also enters in the detailed balance equation. No evidence for resonances are found in the ionization spectra however.

No unambiguous identification of the Cu_A and Cu_B centers in III-V compounds has, to our knowledge, been reported. In early work on GaAs copper was supposed to occupy isolated Ga sites and to be a double acceptor, which was expected from valence considerations. The two dominant levels found were attributed to the double acceptor and when Cu was found to doubly compensate n-type material⁵⁰ the situation seemed clear. However, later results demonstrated that the two levels were due to different centers⁴⁹ and no clear evidence for a double acceptor has been presented. The symmetry of the two centers was investigated using Zeeman analysis of bound exciton luminescence and was found to be C_{3v} and C_{2v} respectively⁴⁹, showing that more complicated defect models are required. The double compensation might be explained by association with donors which is expected to be commonly occurring in material with large Cu and donor concentrations. The compensation studies quoted (ref. 50) are performed on such material. If a Cu-donor associate acts as an acceptor it causes double compensation since it both eliminates one donor and releases one hole.

The identification of the Cu_A and Cu_B centers in GaAs has often been based on studies of the 1.36 and 1.0 eV emission bands often ascribed to these centers. Published attempts to identify these bands are strongly divergent and they have been attributed to Cu_{Ga} and $Cu_{Ga}V_{As}$ respectively¹⁻⁴, $Cu_{Ga}V_{As}$ and $Cu_{Ga}V_{As}Cu_{Ga}$ ⁵, $Cu_{Ga}V_{As}$ and $V_{As}Cu_{Ga}V_{As}$ ⁶ as well as $V_{As}Cu_{Ga}V_{As}$ and $Cu_{Ga}V_{As}$ respectively⁷. Association with As vacancies is the only com-

mon hypothesis among these references. The assignment of the emission bands to Cu_A and Cu_B might not be straightforward however, since isoelectronic centers might lead to erroneous identifications as in the case of GaP.

Copper doped GaP has been less extensively investigated than GaAs. The studies of the Cu-related deep levels have sometimes been confused by emission bands caused by excitons strongly bound to isoelectronic neutral Cu-related centers^{8,9} which are not detected in electrical measurements such as ours. The zero-phonon lines of these bands have energies 2.18 and 1.91 eV. If identifications based on these bands are excluded the published reports give a fairly coherent picture of Cu_A and Cu_B at 0.5 and 0.7 eV above the valence band, with Cu_A giving rise to the 1.65 eV emission band while recombination via Cu_B is non-radiative^{10-15,20}. However, no identifications are proposed and, with the exception below, no indications of association with donors have been reported for these two levels. Indications of at least one Cu-related level not identical with Cu_A but in the same energy region have been seen in luminescence⁵¹ and DLTS spectra of n-type GaP diffused with Cu at elevated temperatures by us show several additional peaks.

An unambiguous identification of Cu_A and Cu_B in the III-Vs is not possible at present. The fact that both centers are present even at very low Cu concentrations probably rules out models including more than one Cu atom per center.

The identification of Cu-donor (Cu-D) associates in GaAs seems to be more straight-forward. Luminescence studies of the $\text{Cu}_{\text{Ga}}\text{Te}_{\text{As}}$ complex indicate a level about 0.20 eV above the valence band¹⁻⁴. The corresponding value obtained from Hall effect measurements is 0.17-0.18 eV^{1,17,18}. A luminescence study of the $\text{Cu}_{\text{Ga}}\text{Si}_{\text{Ga}}$ associate is consistent with a level about 0.28 eV above the valence band².

As mentioned in Sec. II A two levels in InP about 0.3-0.4 eV above the valence band appear after Cu diffusion at somewhat higher temperature or of longer duration. Their positions relative to Cu_A and Cu_B are approximately the same as the corresponding positions of the Cu-D pairs in GaAs. A possible identification of these levels are therefore $\text{Cu}_{\text{In}}^{\text{D}}\text{P}$ and $\text{Cu}_{\text{In}}^{\text{D}}\text{In}$. Levels with similar properties also show up in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ diffused with Cu by us.

In ref. 20 $\text{GaP}:\text{Cu}_B$ is assigned to a Cu-D complex. This is not consistent with the trends discussed above since no evidence has, to our knowledge, been reported for such an identification in other III-Vs. Arguments can be raised against this assignment which is based on a small shift of the σ_p^0 threshold with donor doping. The work is based on a limited number of samples from different sources which might have rather different properties with respect to defects, impurities and strain. Some measurements utilized photoconductors and others pn-junctions where the electric field is roughly 10^4 times larger and might broaden the spectra⁵². The diodes showed "irregularities" with respect to capacitance. If a donor-related shift exists it might be caused by Cu-D complexes closer to the valence band. Far down the ionization edge of Cu_B such complexes could give significant contributions to the photocurrent even at concentrations much smaller than the concentration of Cu_B .

V. Conclusions

A systematic study of the two dominant copper related centers, here denoted Cu_A and Cu_B , in InP and GaAs has been performed using junction space charge spectroscopy. Thermal hole emission rates, photoionization cross sections of holes and electrons, and one electron capture cross section have been measured.

The results, together with published work on GaAs:Cu and GaP:Cu and recent investigations of $\text{Al}_x\text{Ga}_{1-x}\text{As:Cu}$ and $\text{GaAs}_{1-x}\text{P}_x\text{:Cu}$, give a unified description of the role of copper related deep levels in III-V semiconductors. The Cu_A and Cu_B levels are found to have approximately the same positions on an absolute energy scale, i.e. relative to the vacuum level, in both InP, GaAs and GaP, leading us to propose a close similarity between the Cu_A respectively Cu_B centers in these materials. This proposal is supported by the work on $\text{GaAs}_{1-x}\text{P}_x\text{:Cu}_B$ tracing the level from GaAs to GaP. In $\text{Al}_x\text{Ga}_{1-x}\text{As}$ both Cu_A and Cu_B were traced from GaAs to AlAs and found to keep their mutual energy distance.

Further results are consistent with this unified description. The photoionization cross section of holes σ_p^0 for InP:Cu_A exhibits a pronounced structure which is interpreted in terms of Fano resonances due to LO phonon replica of transitions to excited states close to the valence band. A similar but less pronounced structure with weaker phonon coupling has been reported for the corresponding spectrum of GaAs:Cu_A . In InP a feature interpreted as the onset of transitions to the split-off band is also observed.

The ionization spectra of the Cu_B centers show no structure but in InP the optical hole ionization energy is smaller than the corresponding thermal energy. If the high-temperature thermal energy of GaAs:Cu_B is compared with optical data a similar shift is found.

The diffusion behaviour of Cu in InP has also been studied and it is concluded that Cu_A is more easily introduced in the material than Cu_B .

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Appendix

In the original version of the steady-state constant capacitance method²⁹ intense excitation of electrons from the deep level studied into the conduction band establishes a suitable hole occupancy for measuring σ_p^0 . As mentioned in Sec. III B efficient excitation of electrons from the InP:Cu_A level into the conduction band is difficult to achieve due to its small energy distance from the valence band. Therefore band gap light, $h\nu=1.38$ eV, was used in this case to achieve the hole occupancy needed. Since hole capture by this center is much more efficient than electron capture the hole occupancy p_T resulting from gap light only is given by eq.

$$p_T = \frac{c_p p}{c_p p + e_p^r} N_{TT} \quad (1)$$

where c_p is the hole capture constant, p is the free hole concentration (caused by the gap light), e_p^r is the hole emission caused by black-body radiation from warmer objects within the optical aperture of the cryostat, and N_{TT} the total concentration of the Cu_A center.

Simultaneous illumination with low-energy light, $h\nu < 0.7$ eV, changes p_T to

$$p_T + \Delta p_T = \frac{c_p p}{c_p p + e_p^r + e_p^o} N_{TT} \quad (2)$$

where $e_p^o = \sigma_p^0 \phi$ is the optical emission rate of holes. If light intensities are chosen such that $c_p p \gg e_p^o$ then

$$\Delta p_T \approx -e_p^o \frac{c_p p}{(c_p p + e_p^r)^2} N_{TT} \quad (3)$$

Under the condition of constant capacitance this change causes a proportional change in reverse bias which is measured for different photon ener-

gies and thus reveals the σ_p^0 spectrum. An inspection of the equations above shows that moderate black-body radiation is no severe problem in contrast to the case of transient measurements where this radiation limited the sensitivity and thereby the resolution even when careful shielding of the sample was performed.

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Tab. 1 Approximate concentrations N_A and N_B of the two dominant Cu-related deep levels in InP at a junction depth of 7 μm . T is the temperature and t the duration of the Cu diffusion. The detection limit was approximately $1 \cdot 10^{11} \text{ cm}^{-3}$.

T ($^{\circ}\text{C}$)	t (h)	N_A (cm^{-3})	N_B (cm^{-3})
575	2	$1.5 \cdot 10^{13}$	$< 1 \cdot 10^{11}$
600	2	$2 \cdot 10^{14}$	$6 \cdot 10^{11}$
625	2	$3 \cdot 10^{14}$	$5 \cdot 10^{12}$
600	0.25	$5 \cdot 10^{12}$	$< 1 \cdot 10^{11}$
575	20	$2 \cdot 10^{13}$	$2 \cdot 10^{12}$
Reference samples		$5 \cdot 10^{11}$	$< 1 \cdot 10^{11}$

Figure captions

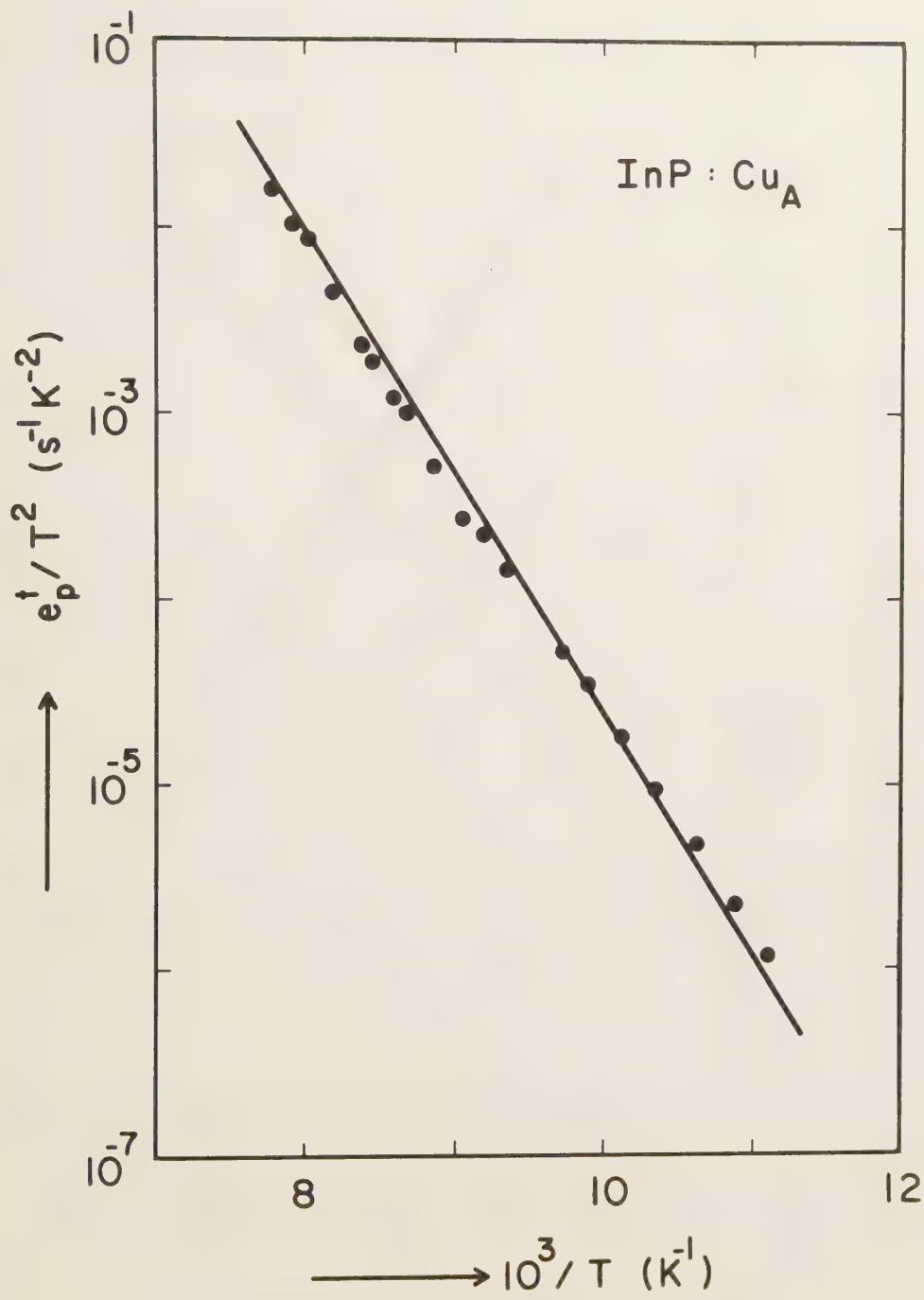
- Fig. 1 Arrhenius plot of e_p^t/T^2 for InP:Cu_A. The higher values, above $1 \cdot 10^{-4} \text{ s}^{-1} \text{ K}^{-2}$, are obtained by DLTS while the lower are obtained by single-shot transients. The slope corresponds to an energy of 0.26 eV.
- Fig. 2 Arrhenius plot of e_p^t/T^2 for InP:Cu_B. The values above $3 \cdot 10^{-5} \text{ s}^{-1} \text{ K}^{-2}$ are obtained by DLTS and the lower by single-shot transients. The slope corresponds to an energy of 0.64 eV.
- Fig. 3 Arrhenius plot of f_p/T^2 for GaAs:Cu_A. f_p is the admittance peak frequency. The slope corresponds to an energy of 0.13 eV.
- Fig. 4 Arrhenius plot of e_p^t/T^2 for GaAs:Cu_B. The values above $2 \cdot 10^{-5} \text{ s}^{-1} \text{ K}^{-2}$ are obtained by DLTS and the lower by single-shot measurements. The slope corresponds to an energy of 0.40 eV.
- Fig. 5 Photoionization cross section of holes σ_p^0 for InP:Cu_A. The periodic structure, marked with arrows in the figure, is interpreted as Fano resonances due to LO phonon replica of discrete electronic transitions. $\hbar\omega_{LO}=42.8 \text{ meV}$.
- Fig. 6 Photoionization cross section of holes σ_p^0 for InP:Cu_B.
- Fig. 7 Photoionization cross section of electrons σ_n^0 for InP:Cu_B.
- Fig. 8 Absorption spectrum of GaAs:Cu_A corresponding to the photoionization cross section of holes σ_p^0 , taken from ref. 30 and 31. E_i is the continuum edge.

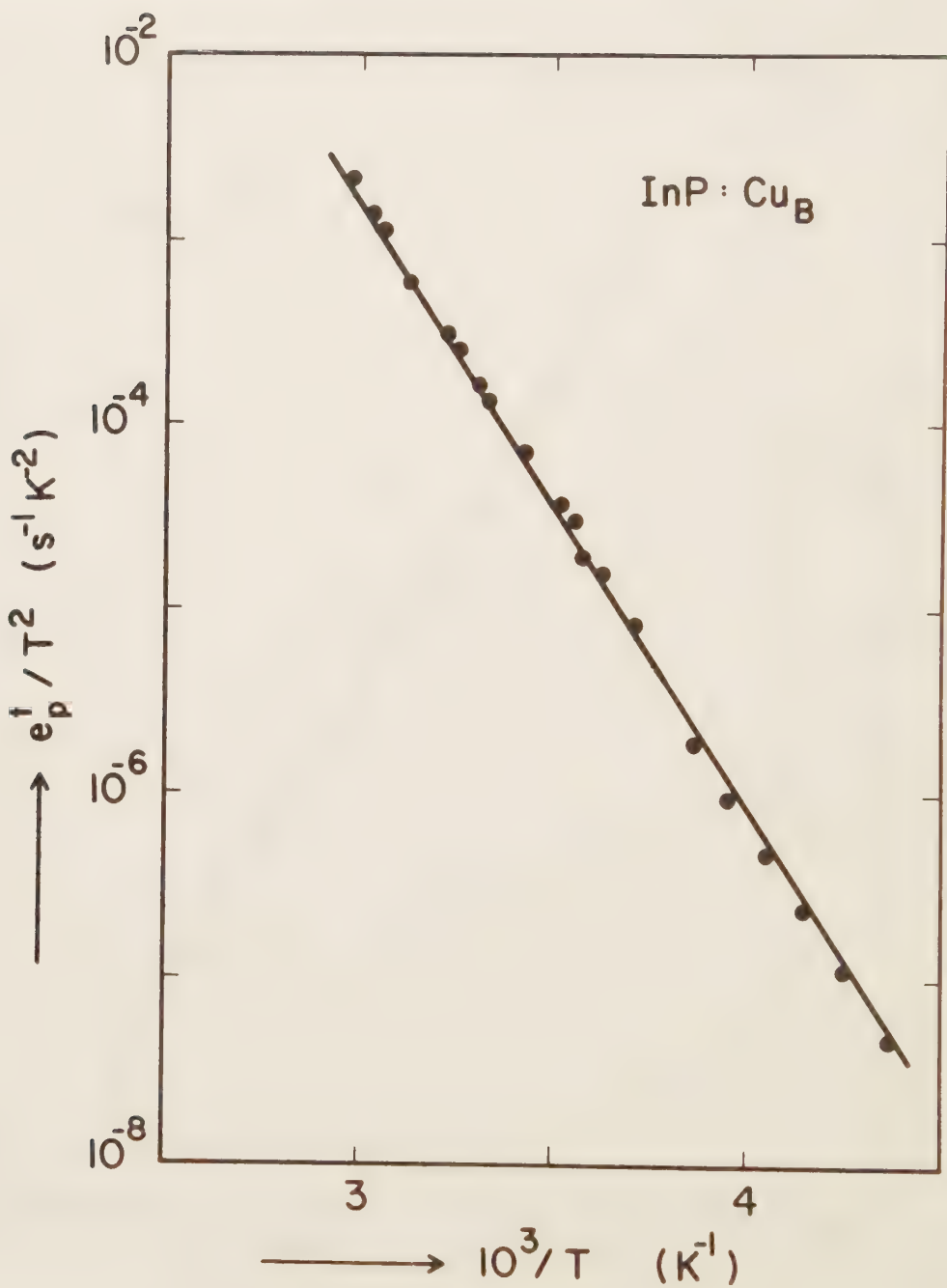
Fig. 9 Photoionization cross section of holes σ_p^0 for GaAs:Cu_B.

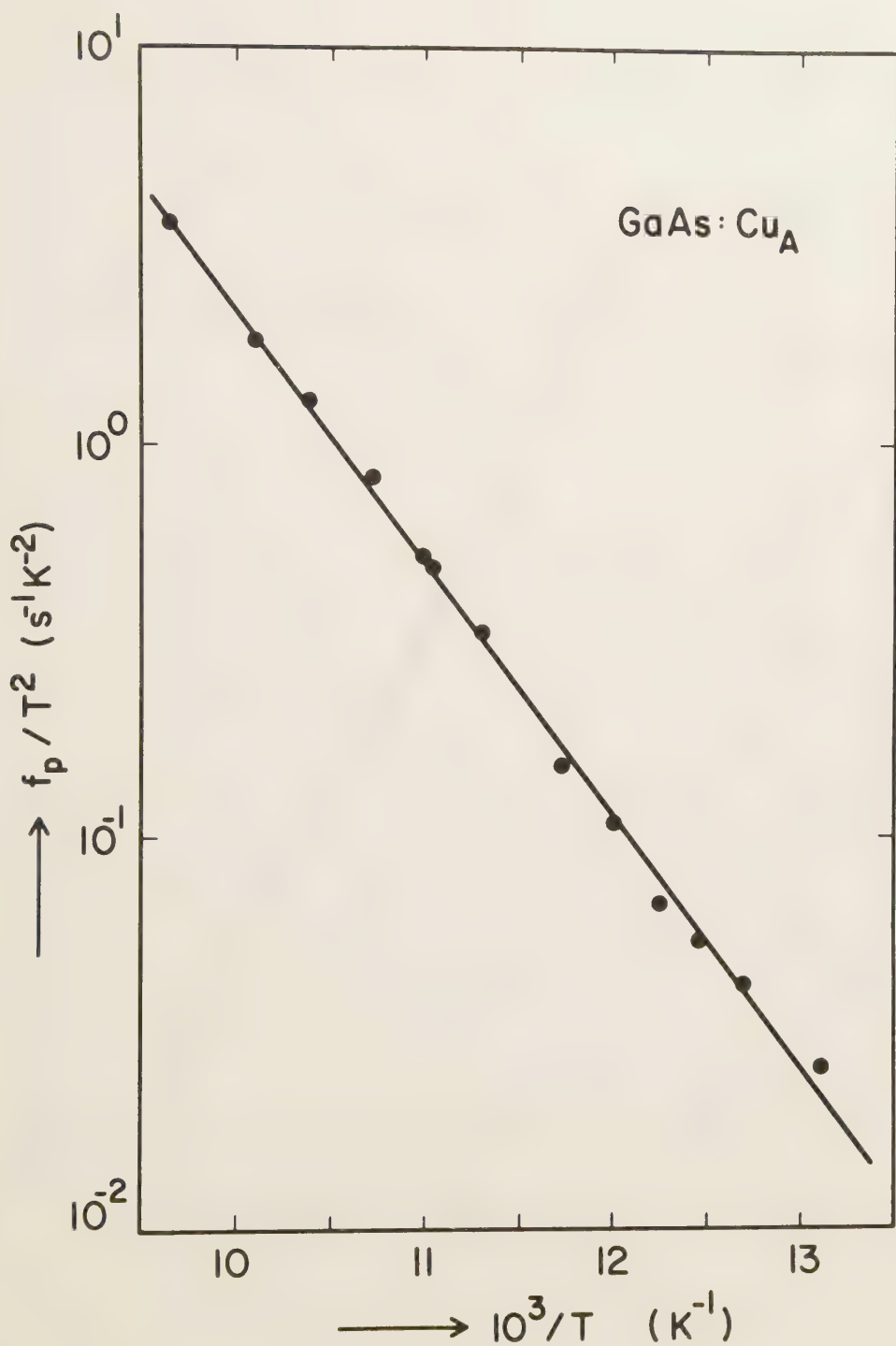
Fig. 10 Photoionization cross section of electrons σ_n^0 for GaAs:Cu_B.

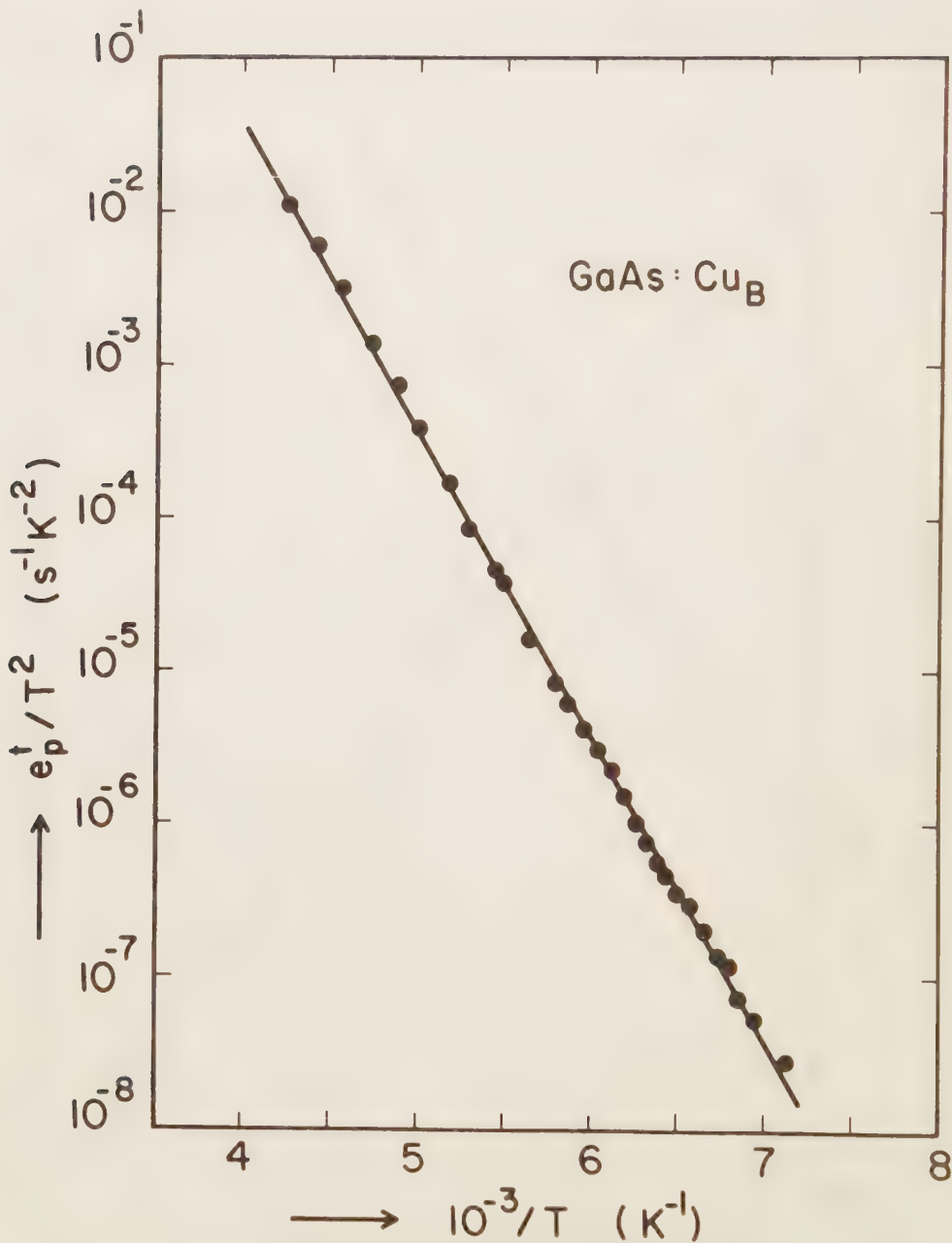
Fig. 11 Arrhenius plot of the electron capture cross section σ_n for InP:Cu_B. The values for $T > 100$ K are obtained by DLTS while the low-temperature values are obtained with the pulse-train technique.

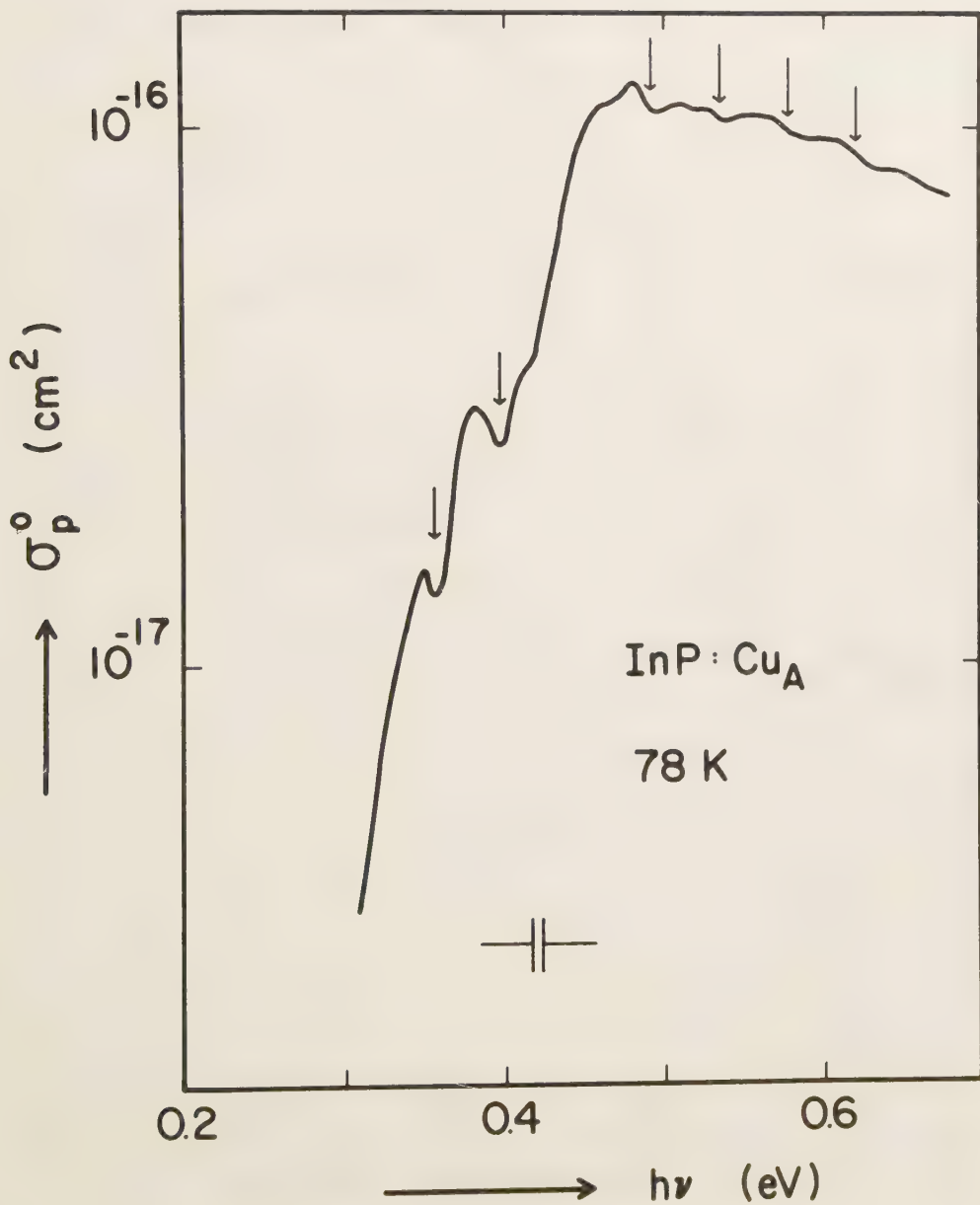
Fig. 12 Summary of the energy levels discussed in this paper.

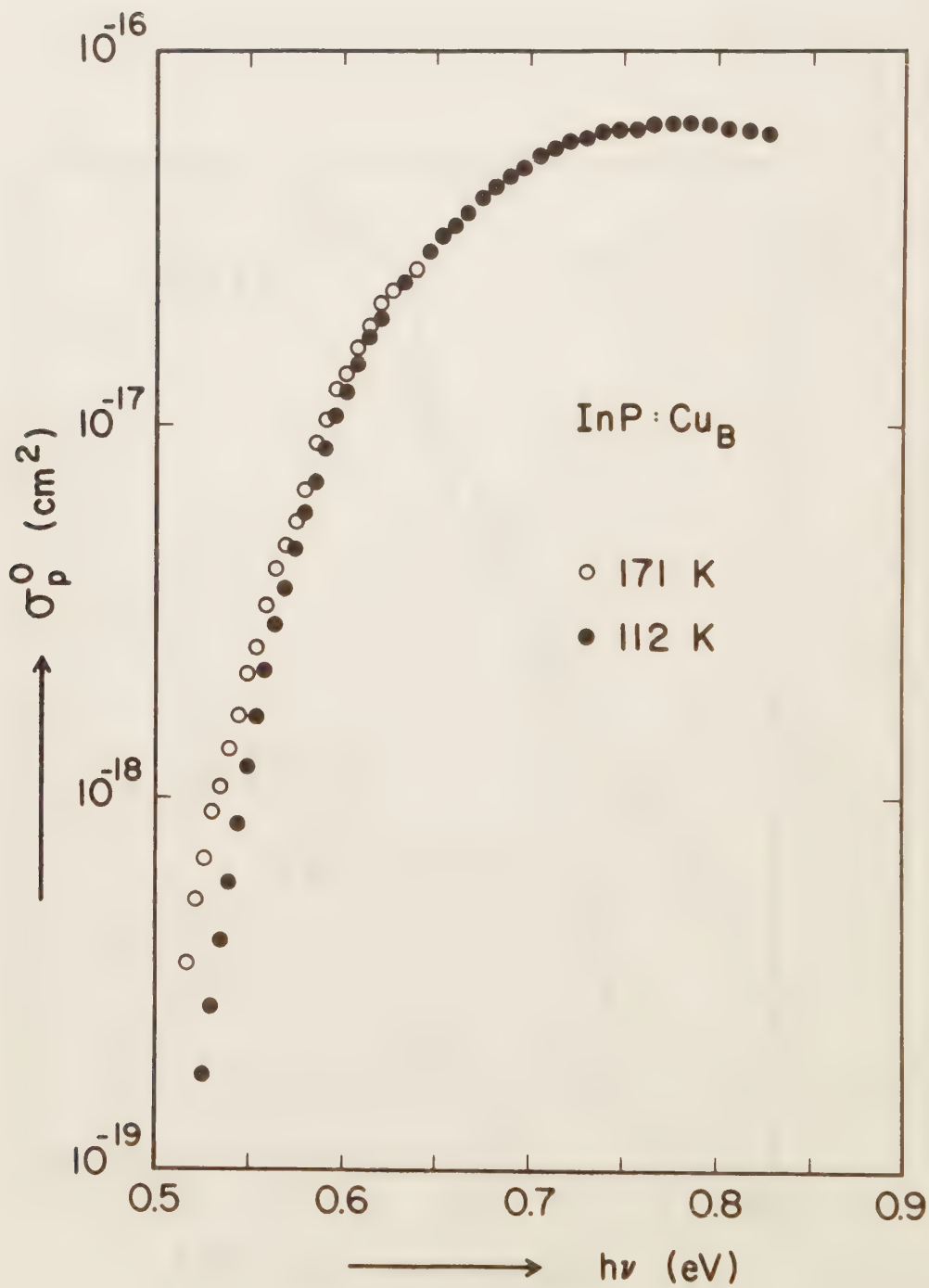


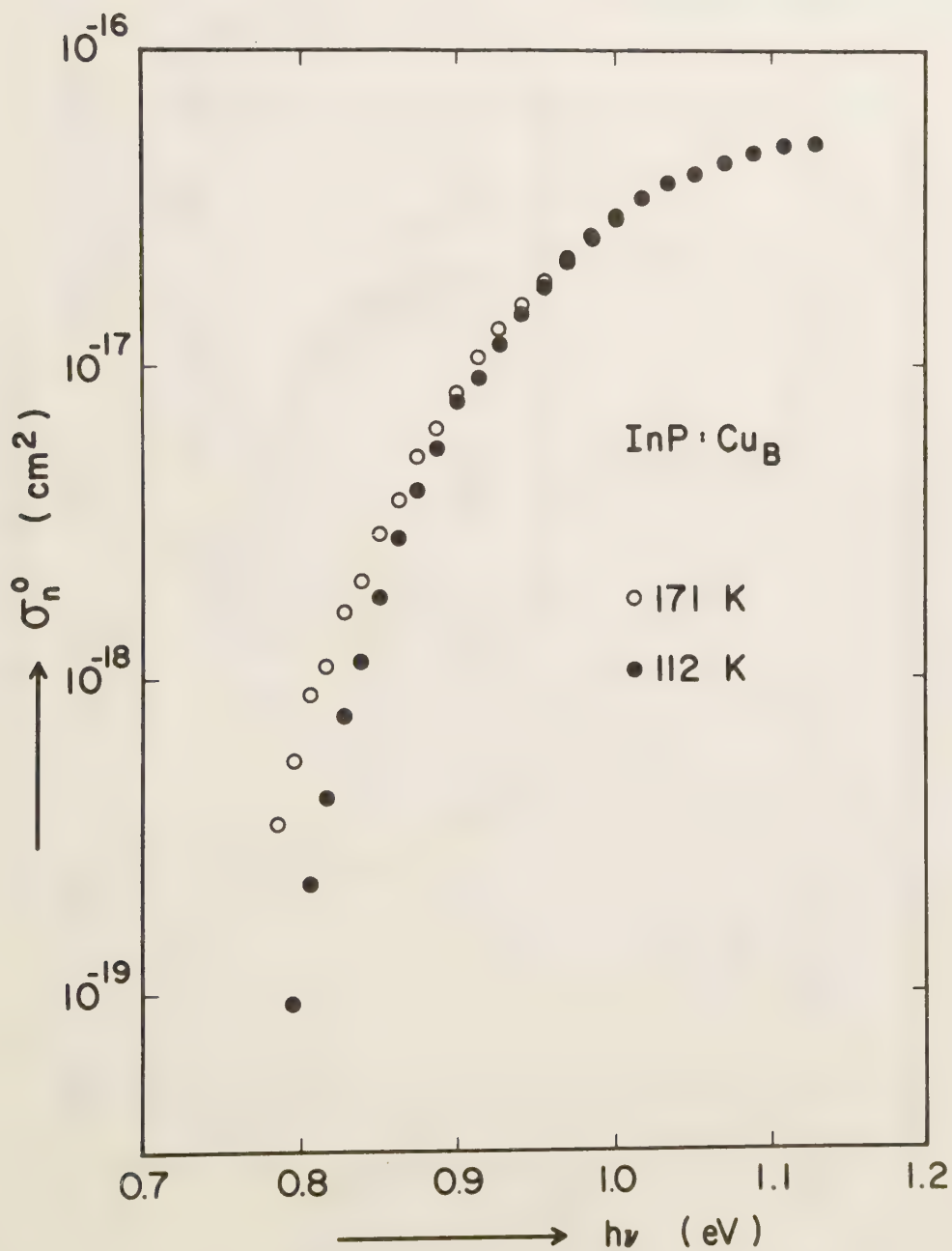


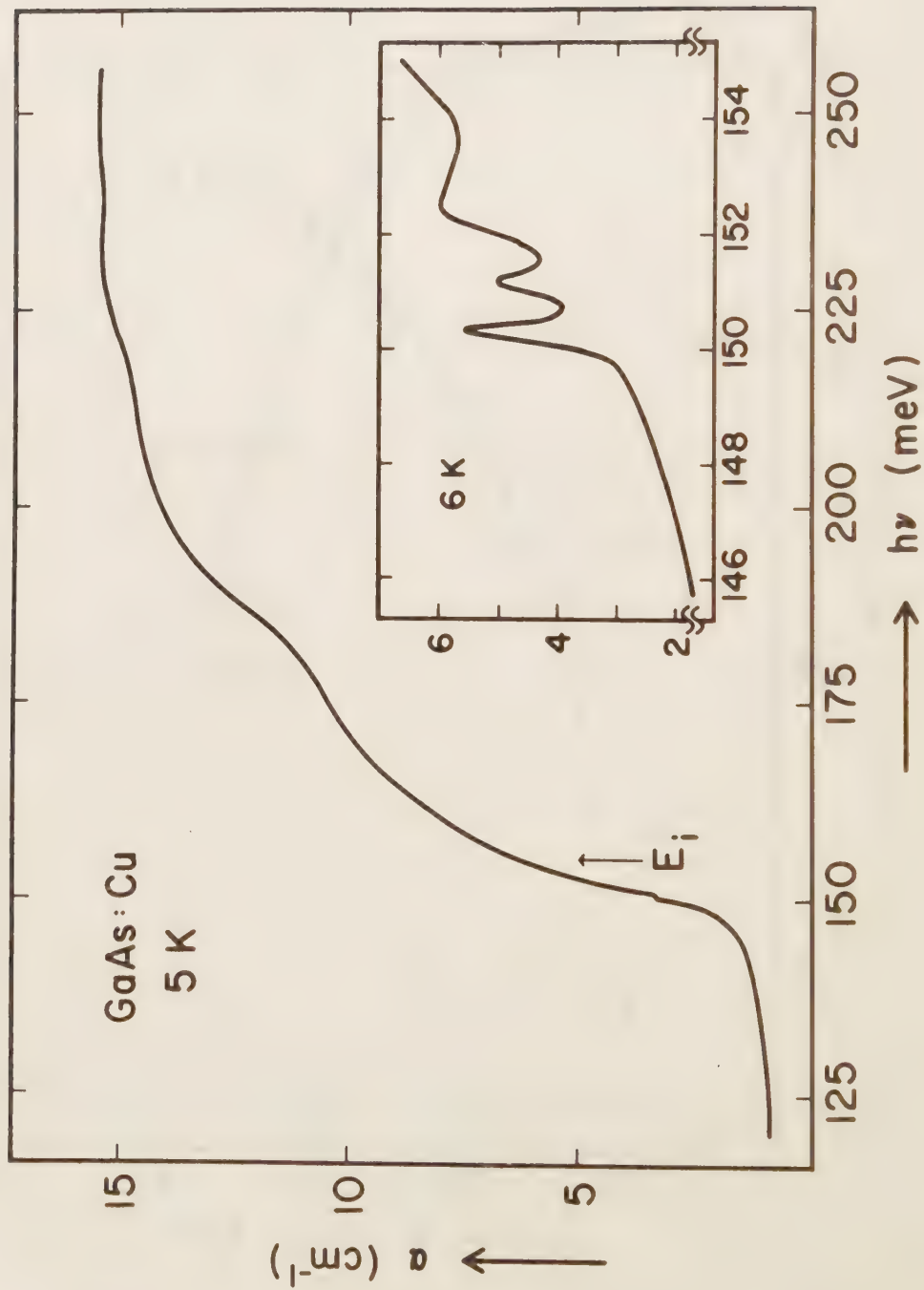


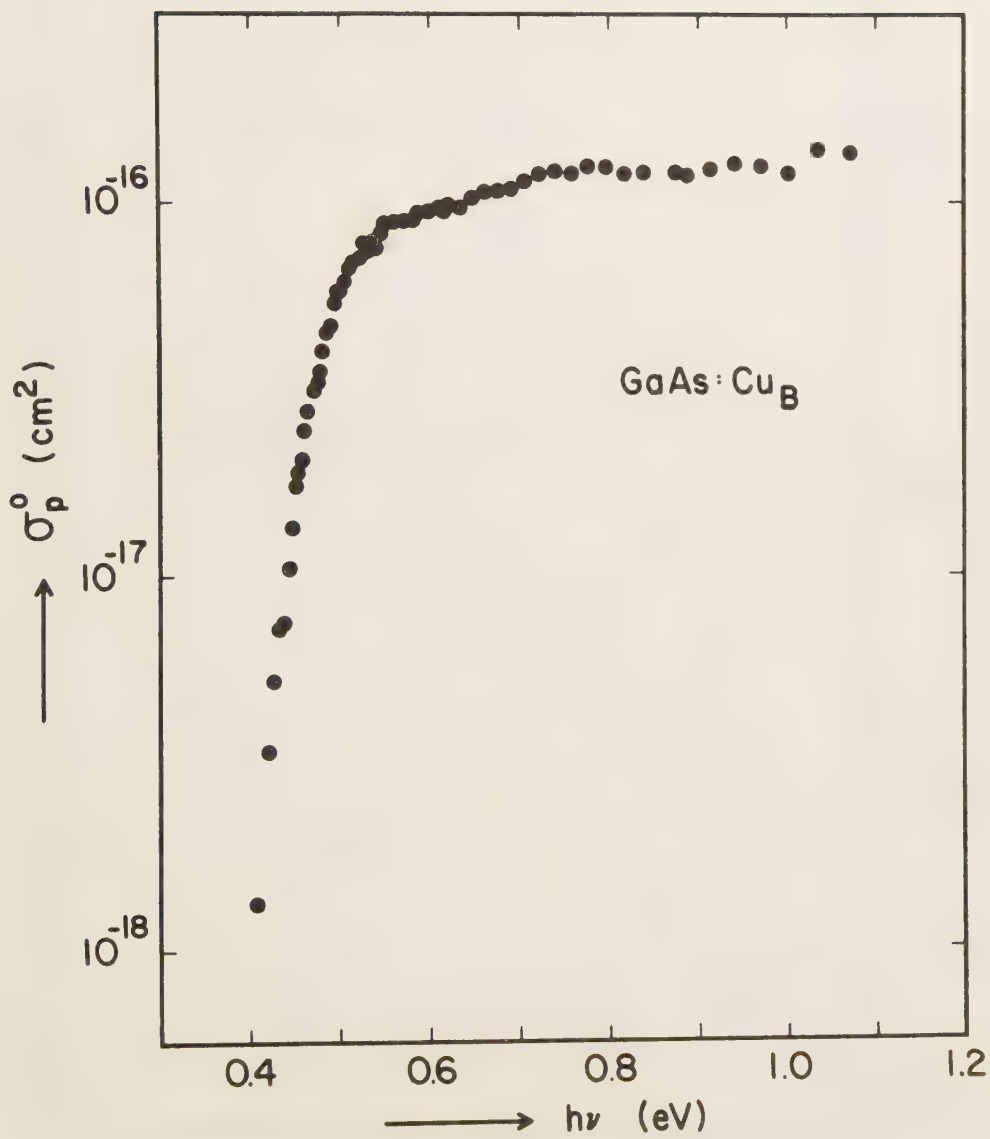


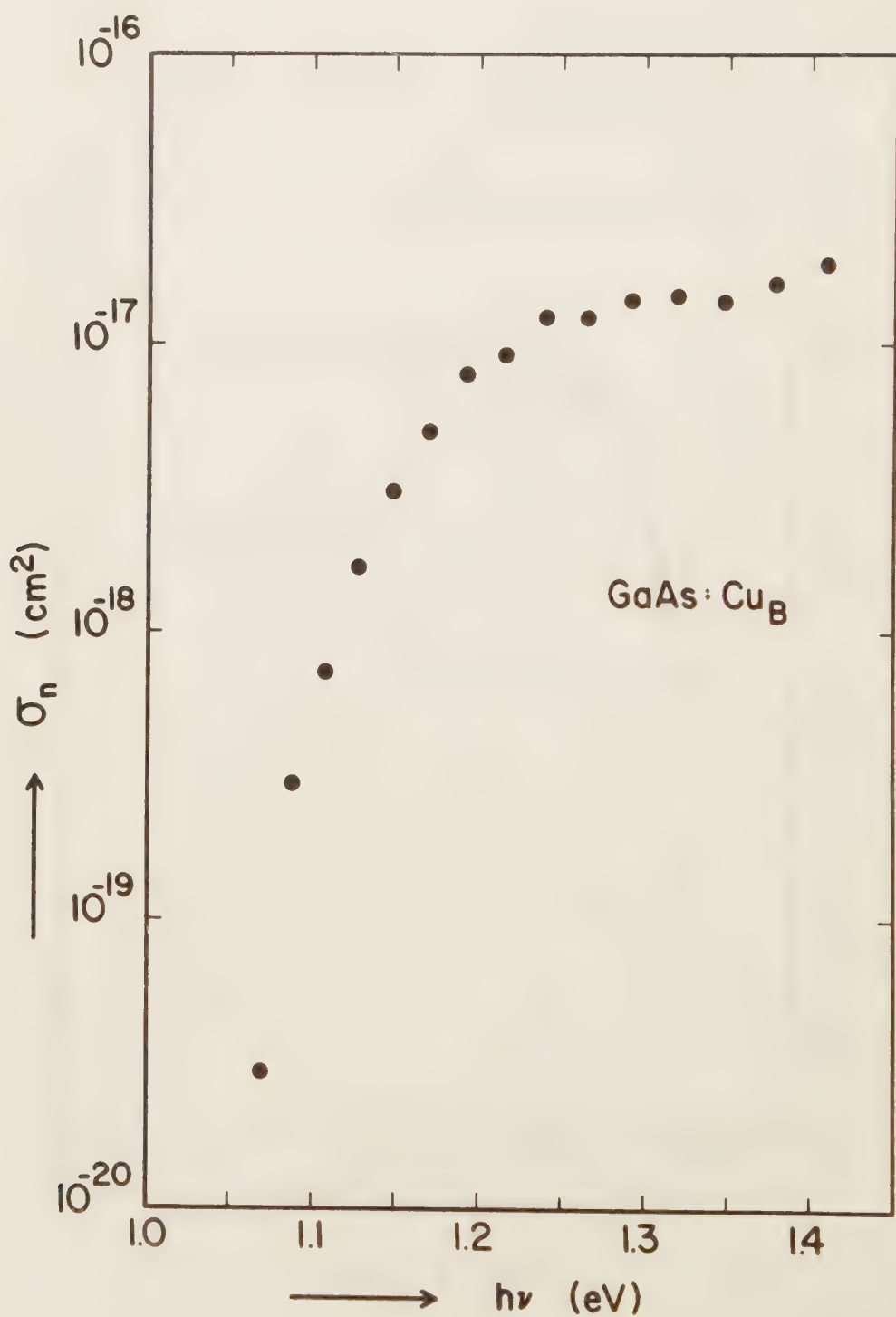


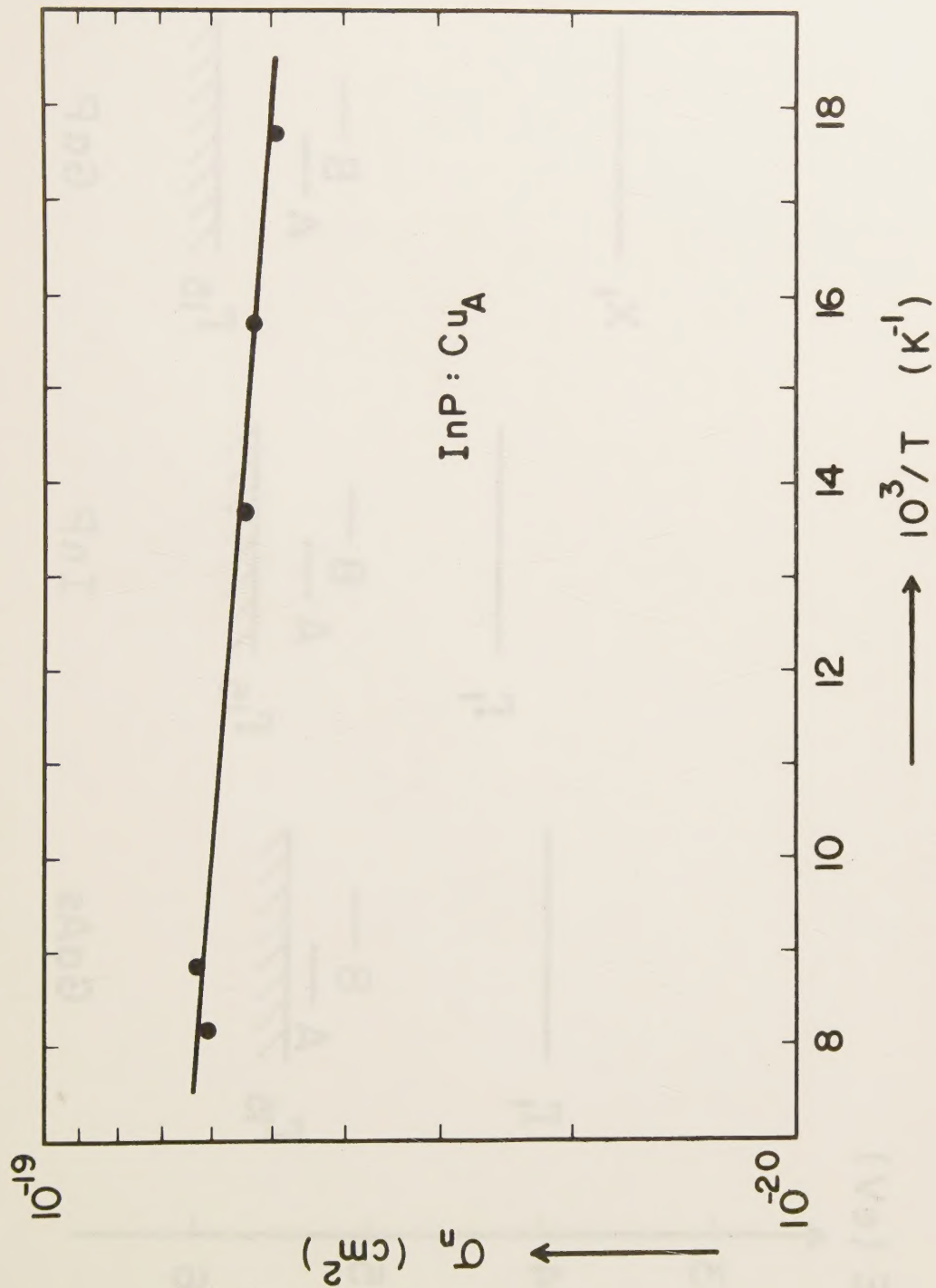












E (eV)

-3

-4

-5

-6

Γ_1

Γ_{15}

A

B

GaAs

Γ_1

Γ_{15}

A

B

InP

X_1

Γ_{15}

A

B

GaP

